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EXHIBIT 22

US006117024A

United States Patent [19]

Dewanjee

[11] Patent Number: 6,117,024

[45] Date of Patent: Sep. 12, 2000

[54] GOLF BALL WITH POLYURETHANE COVER

[75] Inventor: Pijush K. Dewanjee, Oceanside, Calif.

[73] Assignee: Callaway Golf Company, Carlsbad, Calif.

[21] Appl. No.: 09/295,635

[22] Filed: Apr. 20, 1999

[51] Int. Cl.^{7} A63B 37/00

[52] U.S. Cl. 473/351; 473/365; 473/371; 473/372; 473/373; 473/374; 473/375; 473/376

[58] Field of Search 473/371, 372, 473/373, 374, 375, 376, 365

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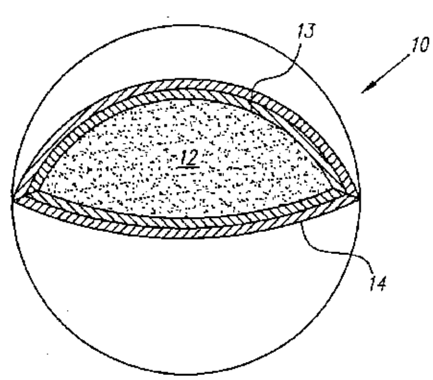
Primary Examiner—Stephen F. Gerrity
Assistant Examiner—Paul D. Kim
Attorney, Agent, or Firm—Michael A. Catania

[57] ABSTRACT

A golf ball having a cover composed of a polyurethane formed from a p-phenylene diisocyanate (PPDI) based polyurethane prepolymer is disclosed herein. The PPDI-based polyurethane prepolymer is formed from a PPDI and a polyol such as polycaprolactone. The PPDI-based polyurethane prepolymer is cured with a curative such as a 1,4 butane diol and glycol. The PPDI-based polyurethane cover may be either thermoset or thermoplastic. The PPDI-based polyurethane cover has a high flexural modulus at a lower hardness which gives a better feel yet maintains good distance, higher Bashore resilience, higher tensile strength, higher tear resistance, improved elongation, and better playability and control. These benefits and improvements are exhibited even though the cover of the present invention is thinner than those of conventional golf balls. The present invention also provides new golf balls having durable thin covers thereby enabling golf balls with large cores. It is well understood that increasing the core diameter of a golf ball generally translates into an increased COR which in turn generally translates into an increased initial velocity and enhanced overall travel distance.

22 Claims, 1 Drawing Sheet



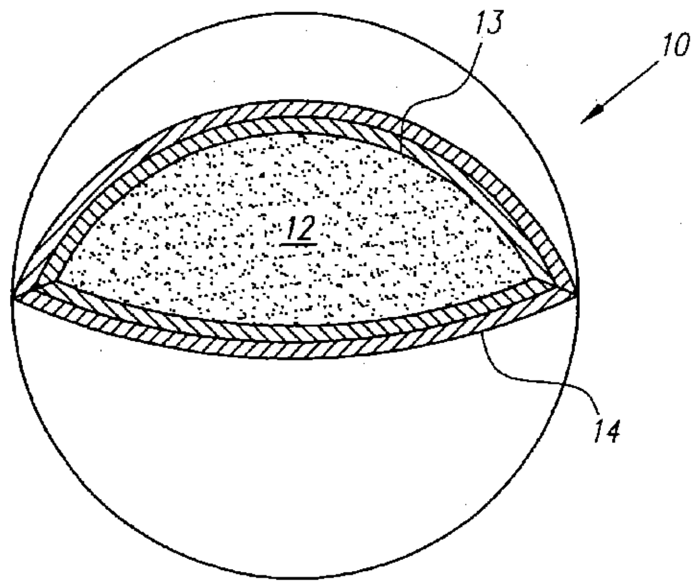


FIG. 1

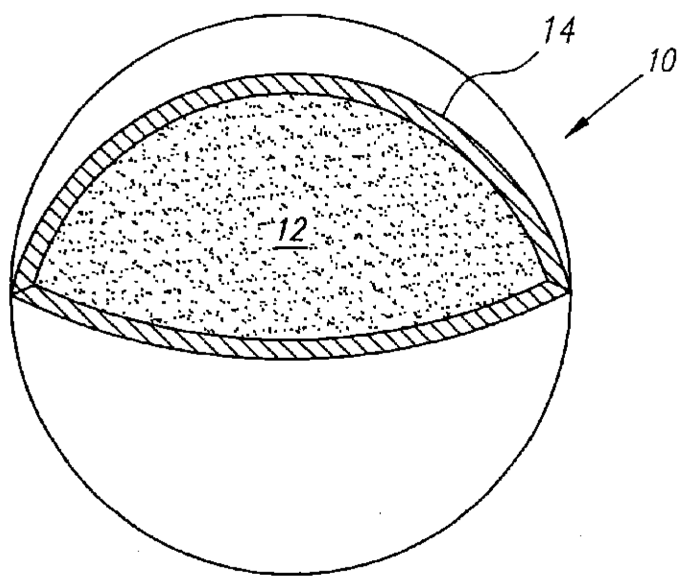


FIG. 2

GOLF BALL WITH POLYURETHANE COVER

CROSS REFERENCES TO RELATED APPLICATIONS

Not Applicable

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

Not Applicable

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to golf balls and golf ball cover materials. More specifically, the present invention relates to golf balls having cover materials containing a polyurethane formed from a para-phenylene diisocyanate prepolymer.

2. Description of the Related Art

Conventionally golf balls are made by molding a cover around a core. The core may be wound or solid. A wound core typically comprises elastic thread wound about a solid or liquid center. Unlike wound cores, solid cores do not include a wound elastic thread layer. Solid cores typically may comprise a single solid piece center or a solid center covered by one or more mantle or boundary layers of material.

The cover may be injection molded, compression molded, or cast over the core. Injection molding typically requires a mold having at least one pair of mold cavities, e.g., a first mold cavity and a second mold cavity, which mate to form a spherical recess. In addition, a mold may include more than one mold cavity pair.

In one exemplary injection molding process each mold cavity may also include retractable positioning pins to hold the core in the spherical center of the mold cavity pair. Once the core is positioned in the first mold cavity, the respective second mold cavity is mated to the first to close the mold. A cover material is then injected into the closed mold. The positioning pins are retracted while the cover material is flowable to allow the material to fill in any holes caused by the pins. When the material is at least partially cured, the covered core is removed from the mold.

As with injection molding, compression molds typically include multiple pairs of mold cavities, each pair comprising first and second mold cavities that mate to form a spherical recess. In one exemplary compression molding process, a cover material is pre-formed into half-shells, which are placed into a respective pair of compression mold cavities. The core is placed between the cover material half-shells and the mold is closed. The core and cover combination is then exposed to heat and pressure, which cause the cover half-shells to combine and form a full cover.

As with the above-referenced processes, a casting process also utilizes pairs of mold cavities. In a casting process, a cover material is introduced into a first mold cavity of each pair. Then, a core is held in position (e.g. by an overhanging vacuum or suction apparatus) to contact the cover material in what will be the spherical center of the mold cavity pair. Once the cover material is at least partially cured (e.g., a point where the core will not substantially move), the core is released, the cover material is introduced into a second mold cavity of each pair, and the mold is closed. The closed mold is then subjected to heat and pressure to cure the cover

material thereby forming a cover on the core. With injection molding, compression molding, and casting, the molding cavities typically include a negative dimple pattern to impart a dimple pattern on the cover during the molding process.

Materials previously used as golf ball covers include balata (natural or synthetic), gutta-percha, ionomeric resins (e.g., DuPont's SURLYN®), and polyurethanes. Balata is the benchmark cover material with respect to sound (i.e. the sound made when the ball is hit by a golf club) and feel (i.e. the sensation imparted to the golfer when hitting the ball). Natural balata is derived from the Bully Gum tree, while synthetic balata is derived from a petroleum compound. Balata is expensive compared to other cover materials, and golf balls covered with balata tend to have poor durability (i.e. poor cut and shear resistance). Gutta percha is derived from the Malaysian sapodilla tree. A golf ball covered with gutta percha is considered to have a harsh sound and feel as compared to balata covered golf balls.

Ionomeric resins, as compared to balata, are typically less expensive and tend to have good durability. However, golf balls having ionomeric resin covers typically have inferior sound and feel, especially as compared to balata covers.

A golf ball with a polyurethane cover generally has greater durability than a golf ball with a balata cover. The polyurethane covered golf ball generally has a better sound and feel than a golf ball with an ionomeric resin cover. Polyurethanes may be thermoset or thermoplastic. Polyurethanes are formed by reacting a prepolymer with a polyfunctional curing agent, such as a polyamine or a polyol. The polyurethane prepolymer is the reaction product of, for example, a diisocyanate and a polyol such as a polyether or a polyester. Several patents describe the use of polyurethanes in golf balls.

Gallagher, U.S. Pat. No. 3,034,791 discloses a polyurethane golf ball cover prepared from the reaction product of poly(tetramethylene ether) glycol and toluene-2,4-diisocyanates (TDI), either pure TDI or an isomeric mixture.

Isaac, U.S. Pat. No. 3,989,568 ("the '568 patent) discloses a polyurethane golf ball cover prepared from prepolymers and curing agents that have different rates of reaction so a partial cure can be made. The '568 patent explains that "the minimum number of reactants is three." Specifically, in '568 patent, two or more polyurethane prepolymers are reacted with at least one curing agent, or at least one polyurethane prepolymer is reacted with two or more curing agents as long as the curing agents have different rates of reaction. The '568 patent also explains that "[o]ne of the great advantages of polyurethane covers made in accordance with the instant invention is that they may be made very thin . . . ", and "[t]here is no limitation on how thick the cover of the present invention may be but it is generally preferred . . . that the cover is no more than about 0.6 inches in thickness." The examples in the '568 patent only disclose golf balls having covers that are about 0.025 inches thick.

Dusbiber, U.S. Pat. No. 4,123,061 ("the '061 patent") discloses a polyurethane golf ball cover prepared from the reaction product of a polyether, a diisocyanate and a curing agent. The '061 patent discloses that the polyether may be polyalkylene ether glycol or polytetramethylene ether glycol. The '061 patent also discloses that the diisocyanate may be TDI, 4,4'-diphenylmethane diisocyanate ("MDI"), and 3,3'-dimethyl-4,4'-biphenylene diisocyanate ("TODI"). Additionally, the '061 patent discloses that the curing agent may be either a polyol (either tri- or tetra-functional and not di-functional) such as triisopropanol amine ("TIPA") or trimethoylol propane ("TMP"), or an amine-type having at

least two reactive amine groups such as: 3,3'dichlorobenzidene; 3,3'dichloro 4,4'diamino diphenyl methane ("MOCA"); N,N,N',N'tetrakis (2-hydroxy propyl) ethylene diamine; or Uniroyal's Curalon L which is an aromatic diamine mixture.

Hewitt, et al., U.S. Pat. No. 4,248,432 ("the '432 patent") discloses a thermoplastic polyesterurethane golf ball cover formed from a reaction product of a polyester glycol (molecular weight of 800–1500) (aliphatic diol and an aliphatic dicarboxylic acid) with a para-phenylene diisocyanate ("PPDI") or cyclohexane diisocyanate in the substantial absence of curing or crosslinking agents. The '432 patent teaches against the use of chain extenders in making polyurethanes. The '432 patent states, "when small amounts of butanediol-1,4 are mixed with a polyester . . . the addition results in polyurethanes that do not have the desired balance of properties to provide good golf ball covers. Similarly, the use of curing or crosslinking agents is not desired . . . "

Holloway, U.S. Pat. No. 4,349,657 ("the '657 patent") discloses a method for preparing polyester urethanes with PPDI by reacting a polyester (e.g. prepared from aliphatic glycols having 2–8 carbons reacted with aliphatic dicarboxylic acids having 4–10 carbons) with a molar excess of PPDI to obtain an isocyanate-terminated polyester urethane (in liquid form and stable at reaction temperatures), and then reacting the polyester urethane with additional polyester. The '657 patent claims that the benefit of this new process is the fact that a continuous commercial process is possible without stability problems. The '657 patent further describes a suitable use for the resultant material to be golf ball covers.

Kolycheck, U.S. Pat. No. 4,442,282 ("the '282 patent") discloses a thermoplastic polyesterurethane golf ball cover formed by reacting a 1,12-dodecandioc acid polyester (molecular weight of about 1500–5000) with MDI. The '282 patent teaches that "[t]he use of chain extenders in making the polyurethanes is not normally desired and may result in polyurethanes that do not have the desired balance of properties to provide good golf ball covers. Similarly, the use of curing or crosslinking agents is not desired . . . "

Wu, U.S. Pat. No. 5,334,673 ("the '673 patent") discloses a polyurethane prepolymer cured with a slow-reacting curing agent selected from slow-reacting polyamine curing agents and difunctional glycols (i.e., 3,5-dimethylthio-2,4-toluenediamine, 3,5-dimethylthio-2,6-toluenediamine, N,N'-dialkyldiamino diphenyl methane, trimethyleneglycol-di-p-aminobenzoate, polytetramethyleneoxide-di-p-aminobenzoate, 1,4-butanediol, 2,3-butanediol, 2,3-dimethyl-2,3-butanediol, ethylene glycol, and mixtures of the same). The polyurethane prepolymer in the '673 patent is disclosed as made from a polyol (e.g., polyether, polyester, or polylactone) and a diisocyanate such as MDI or TODI. The polyether polyols disclosed in the '673 patent are polytetramethylene ether glycol, poly(oxypropylene) glycol, and polybutadiene glycol. The polyester polyols disclosed in the '673 patent are polyethylene adipate glycol, polyethylene propylene adipate glycol, and polybutylene adipate glycol. The polylactone polyols disclosed in the '673 patent are diethylene glycol initiated caprolactone, 1,4-butanediol initiated caprolactone, trimethylol propane initiated caprolactone, and neopentyl glycol initiated caprolactone.

Cavallaro, et al., U.S. Pat. No. 5,688,191 discloses a golf ball having core, mantle layer and cover, wherein the mantle layer is either a vulcanized thermoplastic elastomer, functionalized styrene-butadiene elastomer, thermoplastic polyurethane, metallocene polymer or blends of the same and thermoset materials.

Wu, et al., U.S. Pat. No. 5,692,974 discloses golf balls having covers and cores that incorporate urethane ionomers (i.e. using an alkylating agent to introduce ionic interactions in the polyurethane and thereby produce cationic type ionomers).

Sullivan, et al., U.S. Pat. No. 5,803,831 ("the '831 patent") discloses a golf ball having a multi-layer cover wherein the inner cover layer has a hardness of at least 65 Shore D and the outer cover layer has a hardness of 55 Shore D or less, and more preferably 48 Shore D or less. The '831 patent explains that this dual layer construction provides a golf ball having soft feel and high spin on short shots, and good distance and average spin on long shots. The '831 patent provides that the inner cover layer can be made from high or low acid ionomers such as SURLYN®, ESCOR® or IOTEK®, or blends of the same, nonionomeric thermoplastic material such as metallocene catalyzed polyolefins or polyamides, polyamide/ionomer blends, polyphenylene ether/ionomer blends, etc., (having a Shore D hardness of at least 60 and a flex modulus of more than 30000 psi), thermoplastic or thermosetting polyurethanes, polyester elastomers (e.g. HYTREL®), or polyester amides (e.g. PEBEX®), or blends of these materials. The '831 patent also provides that the outer cover layer can be made from soft low modulus (i.e. 1000–10000 psi) material such as low-acid ionomers, ionomeric blends, non-ionomeric thermoplastic or thermosetting materials such as polyolefins, polyurethane (e.g. thermoplastic polyurethanes like TEXIN®, PELETHANE®, and thermoset polyurethanes like those disclosed in Wu, U.S. Pat. No. 5,334,673), polyester elastomer (e.g. HYTREL®), or polyester amide (e.g. PEBEX®), or a blend of these materials.

Hebert, et al., U.S. Pat. No. 5,885,172 ("the '172 patent") discloses a multilayer golf ball giving a "progressive performance" (i.e. different performance characteristics when struck with different clubs at different head speeds and loft angles) and having an outer cover layer formed of a thermoset material with a thickness of less than 0.05 inches and an inner cover layer formed of a high flexural modulus material. The '172 patent provides that the outer cover is made from polyurethane ionomers as described in Wu, et al., U.S. Pat. No. 5,692,974, or thermoset polyurethanes such as TDI or methylenebis-(4-cyclohexyl isocyanate) ("HMDI"), or a polyol cured with a polyamine (e.g. methylenedianiline (MDA)), or with a trifunctional glycol (e.g., N,N,N',N'-tetrakis(2-hydroxpropyl)ethylenediamine). The '172 also provides that the inner cover has a Shore D hardness of 65–80, a flexural modulus of at least about 65,000 psi, and a thickness of about 0.020–0.045 inches. Exemplary materials for the inner cover are ionomers, polyurethanes, polyetheresters (e.g. HYTREL®), polyetheramides (e.g., PEBEX®), polyesters, dynamically vulcanized elastomers, functionalized styrene-butadiene elastomer, metallocene polymer, blends of these materials, nylon or acrylonitrile-butadiene-styrene copolymer.

Wu, U.S. Pat. No. 5,484,870 ("the '870 patent") discloses golf balls having covers composed of a polyurea composition. The polyurea composition disclosed in the '870 patent is a reaction product of an organic isocyanate having at least two functional groups and an organic amine having at least two functional groups. One of the organic isocyanates disclosed by the '870 patent is PPDI.

Nesbitt, U.S. Pat. No. 4,431,193 ("the '193 patent") discloses a multi-layered golf ball having a two-layer cover. The '193 patent describes a golf ball having a cover composed of an inner layer of hard high flexural modulus resinous material, cellular or foam composition having a

high coefficient of restitution, and an outer layer of a comparatively soft low flexural modulus resinous material, cellular or foam composition. The '193 patent also describes that the inner cover layer is preferably about 0.02–0.07 inches thick and the outer cover layer is preferably about 0.02–0.10 inches thick. The '193 patent explains that this dual layer cover construction provides an increased coefficient of restitution and a balata feel. However, each layer of the cover of the '193 patent is composed of an ionomer (e.g. SURLYN®), and therefore, the golf balls suffer from the performance deficiencies described above.

Although the prior art has disclosed golf ball covers composed of many different materials, none of these golf balls have proven completely satisfactory. Dissatisfaction, for example, remains with processing and manufacturing the balls, and with the balls' durability and performance.

Specifically, with respect to processing, prior materials are not user friendly because certain starting materials may be unhealthful, such as diamines and isocyanides. In addition, prior balls using such materials are generally wound balls. Wound balls have tolerances that are more difficult to control due to core sizes and/or windings sizes, and therefore, require thicker cover layers to account for the manufacturing tolerances. With respect to durability problems, prior polyurethane covered balls, because they are wound balls, tend to lose compression and initial velocity due to the windings relaxing over time and use. With respect to performance problems, prior balls, as a general rule, tend to have smaller cores that result in shorter flight distances.

Although many golf balls having a polyurethane cover have been provided by the prior art, these golf balls have failed to capture the sound and feel of balata while providing a golf ball with the durability of an ionomer. One material of interest disclosed in the golf ball prior art is PPDI. However, the golf ball prior art has been unable to capture its full potential, and thus PPDI has been ignored or utilized as just another diisocyanate in conventional polyurethane formulations. Thermoplastic and castable elastomer polyurethanes from PPDI are known for use in high performance parts such as, for example, seals and gaskets, tires and wheels, and pump parts. See, e.g., A. Singh, "p-Phenylene Diisocyanate Based Polyurethane Elastomers", Advances in Urethane Science and Technology Vol. 13 (Eds. K. Frisch & D. Klempher, 1996). Several patents outside of the golf ball industry also disclose forming polyurethanes from PPDI.

Kolycheck, U.S. Pat. No. 5,159,053 ("the '053 patent") discloses a thermoplastic polyurethane having electrostatic dissipative properties, an average molecular weight of about 60,000–500,000, and composed of a hydroxyl terminated ethylene ether oligomer glycol intermediate (i.e. a polyethylene glycol) reacted with a non-hindered diisocyanate (e.g. PPDI, MDI, 1,5-naphthalene diisocyanate ("NDI"), m-xylene diisocyanate ("XDI"), 1,4-cyclohexyl diisocyanate ("CHDI") and an extender glycol (e.g. diethylene glycol, 1,3-propane diol, 1,4-butane diol, 1,5-pentane diol, and 1,6-hexane diol) to produce a high molecular weight thermoplastic polyurethane. The '053 patent describes the material as "useful as an elastomeric melt or binder in a fabric reinforced flexible fuel tank" and "as sheets or films, fuel handling [devices] including vapor return equipment and fuel lines, business equipment, coatings for floors such as clean rooms and construction, floorings, mats, electronic packaging and housings, chip holders, chip rails, tote bins and tote bin tops and medical applications."

Ohbuchi, et al., U.S. Pat. No. 5,066,762 ("the '762 patent") discloses a thermoplastic polyurethane resin obtained by reacting a PPDI, hydroxyl terminated poly (hexamethylene carbonate) polyol (obtained by reacting 1,6-hexane glycol with diphenyl carbonate, diethyl carbonate, ethylene carbonate, etc., and a triol) and a short chain polyol (e.g., ethylene glycol, 1,3-propylene glycol, 1,4-butane diol, neopentyl glycol, 3-methyl-1,5-pentane diol, p-xylene glycol, 1,4-bis-(β-hydroxyethoxy)benzene, 1,3-bis-(β-hydroxyethoxy)benzene, cyclohexane,1,4-dimethanol, octane-1,8-diol, decane-1,10-diol, etc., or a mixture) as an extending agent. The '762 patent also discloses that the poly(hexamethylene carbonate) polyol can be mixed with poly(butylene adipate) polyol, polycaprolactone polyol, poly(hexamethylene adipate) polyol, etc., but that the material's performance is adversely affected by such an addition. The '762 patent further explains that a triol can be included in the diol to aid in crosslinking if needed. Asserted material improvements are in hydrolysis resistance, heat deterioration resistance, temperature dependency and compression set. The '762 patent explains that suitable uses for the material are "for the production of articles of small size such as precise parts including packing, sound-damping gear, bearing, joint, parts for precise machines, automotive parts, electronic instrument parts, etc., . . . belt[s], hose[s], tube[s], sheet[s], film[s], etc. by extrusion [molding]."

Kolycheck U.S. Pat. No. 5,047,495 ("the '495 patent") discloses a polyurethane reinforced fabric molded flexible fuel tank. The fuel tank of the '495 patent is composed of a high molecular weight thermoplastic polyurethane polymer binder formed from the reaction product of an ethylene ether oligomer glycol intermediate (a hydroxyl terminated diethylene glycol aliphatic linear polyester, or a polyethylene glycol) and a non-hindered diisocyanate (e.g. PPDI, MDI, NDI, XDI or CHDI) and an extender glycol (e.g. diethylene glycol, 1,3-propane diol, 1,4-butane diol, 1,5-pentane diol, and 1,6-hexane diol). The '495 patent describes the material as having good fuel resistance and as useful in making resilient fuel tanks and containers when combined with fibrous mat reinforcement material.

Watabe, et al., U.S. Pat. No. 4.062,825 discloses a polyurethane prepared by mixing prepolymer (e.g. PPDI among many others) with finely divided acidic silica particles and curative thereby providing a polyurethane having high tear strength.

However, none of these polyurethanes have proven satisfactory for use in golf balls or, more particularly, as golf ball covers. For example, such materials tend to be too 'clicky' (i.e. with respect to sound) and not sufficiently abrasion resistant. In addition, such materials are not sufficiently durable to make golf ball covers thinner than about 0.05 inches. Furthermore, a thermoplastic with reinforced fabric, as may be suggested by Kolycheck, should not be used in golf ball materials because such an addition would adversely affect at least some of those physical properties of the thermoplastic which are particularly desirable for golf balls such as COR and rebound. These patents are not the denouement of the use of PPDI in the formation of a polyurethane. Thus, there remains a need for a golf ball that has the sound and feel of a golf ball with a balata cover, while providing the outstanding durability of a golf ball with an ionomer cover.

BRIEF SUMMARY OF THE INVENTION

The present invention provides a golf ball with the sound and feel of a golf ball with a balata cover, and the durability of a golf ball with an ionomer cover. The present invention is able to accomplish this by providing a novel polyurethane system that is particularly useful as a golf ball cover material.

The material of the present invention does not exhibit the above-described deficiencies in the prior polyurethane systems. The material of the present invention provides a golf ball cover having improved durability and improved sound and feel over the prior golf ball covers. In addition, golf balls including a cover made of the material of the present invention have comparable or higher COR, and higher rebound at similar or lower hardness. Therefore, a golf ball cover of the present invention contributes to good durability, increased overall travel distance, better playability and control, and enhanced sound and feel of a golf ball including such a cover.

Furthermore, the present invention provides a polyurethane system that allows post-curing at higher temperatures than is provided in the prior art. Higher temperature post-curing enables use of a very thin cover layer and toughens the material making it more durable. Such post-curing also provides improved Bayshore rebound, improved tensile strength, and improved tear resistance and elongation, as compared to prior systems.

One aspect of the present invention is a golf ball cover composed of a polyurethane system formed from a PPDI-based prepolymer. The PPDI-based prepolymer is formed by a reaction of PPDI with an ester polyol, a polyether polyol or a blend of more than one of these compounds. Preferably, the compound has a molecular weight range of about 250–3500. A preferred compound is polycaprolactone. The PPDI prepolymer is then cured with an agent for a set period of time. The agent may be a diol (e.g., 1,4 butane diol, trimethylpropanol, etc.), a mixture of diols (e.g., 1,4 butane diol and ethylene glycol, or other suitable glycols), a hydroquinone, a mixture of hydroquinones, a triol, a mixture of triols, a diamine, a mixtures of diamines, an oligomeric diamine, or a blend of some or all of these materials. The polyurethane system may be either thermoset (i.e. functional in cast manufacturing) or thermoplastic (i.e. functional in injection molding).

Polyurethane systems based on PPDI give higher flexural modulus when compared to polyurethane systems based on other materials such as MDI and TDI. This higher flexural modulus for PPDI is believed to be due to the more uniform hard segment distribution of the PPDI-based material. In addition, it is believed that the rigid rod-like structure of PPDI, as compared to the more bulky or hindered structures of MDI and TDI, provide PPDI-based polyurethane systems relatively superior physical properties. Some of these physical properties include increased Bashore resilience, increased tensile strength, increase tear resistance, improved elongation, and a lower tan δ value. The tan δ value measures the amount of energy a material loses as heat upon a high distortion or impact event (i.e. hysteresis). See, B. S. Lombardo, et al., "Advances in PPDI Prepolymer Technology", Uniroyal Chemical Company, Inc., Middlebury, Conn. 06749, which is hereby incorporated by reference as if fully set forth herein.

Another aspect of the present invention is a golf ball including a core with a diameter of about 1.35–1.70 inches, or more preferably between about 1.40–1.65 inches, or most preferably between about 1.45–1.60 inches, and a polyurethane cover having a thickness of between about 0.02–0.09 inches, or more preferably between about 0.02–0.065 inches, or most preferably between about 0.02–0.04 inches.

Another aspect of the present invention is a golf ball with a core having a diameter of about 1.35–1.7 inches, or more preferably between about 1.4–1.65 inches, or most preferably between about 1.45–1.6 inches, one or more boundary or mantle layer(s) having a total combined thickness of between about 0.02–0.09 inches, or more preferably between about 0.02–0.075 inches, or most preferably between about 0.02–0.067 inches, and a polyurethane cover having a thickness of between about 0.02–0.09 inches, or more preferably between about 0.02–0.065 inches, and most preferably between about 0.02–0.04 inches.

Another aspect of the present invention is a golf ball having a polybutadiene inner core with a diameter of between about 1.35–1.7 inches, a thermoplastic boundary or mantle layer having a wall thickness of between about 0.02–0.09 inches, and a polyurethane cover having a wall thickness of between about 0.02–0.09 inches. It is preferred that the ratio of core diameter to the wall thickness of the cover be in the range of about 15:1 to 90:1, and more preferably in the range of about 25:1 to 77.5:1, and most preferably in the range of about 35:1 to 65:1. For example, for a ball having an overall diameter of about 1.68 inches, one embodiment most preferably has an inner core having a diameter of about 1.45–1.6 inches, a mantle layer having a thickness of about 0.02–0.067 inches, and a cover having a thickness of about 0.02–0.04 inches. In another example, for a ball having an overall diameter of about 1.8 inches, a preferred embodiment has an inner core with a diameter of about 1.6–1.72 inches, a boundary layer having a wall thickness of about 0.02–0.067 inches, and a cover with a thickness of about 0.02–0.04 inches.

Another aspect of the present invention is a golf ball having a solid core of an elastomeric material having a diameter of between about 1.35–1.70 inches, and a PGA compression of between about 50–80, a boundary layer of a thermoplastic material having a hardness of between about 52–65 Shore D, a flexural modulus of between about 25,000–65,000 psi, and a wall thickness of between about 0.02–0.09 inches, and a cover having a hardness of between about 45–60 Shore D, a flexural modulus of between about 12,000–35,000 psi, a Bashore resilience of between about 57–65, a tensile strength of between about 5900–7500 psi, and a wall thickness of between about 0.02–0.09 inches.

It is a primary object of the present invention to provide a golf ball having a cover made from a new polyurethane system.

Other objects and features of the present invention will become apparent from consideration of the following description taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

FIG. 1 illustrates a perspective view of a golf ball of the present invention including cut-away portion showing a core, a boundary layer, and a cover.

FIG. 2 illustrates a perspective view of a golf ball of the present invention including a cut-away portion core and a cover.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a new polyurethane system which is particularly useful as a golf ball cover material having improved durability, improved sound and feel, higher COR, higher flexural modulus at lower hardness, a lower tan δ, and higher rebound, and, therefore, contributes to an increased initial velocity, enhanced overall travel distance, and better playability and control.

Golf balls of the present invention generally include a solid core and a cover. One or more boundary or mantle layers may optionally be provided between the core and cover. In the preferred embodiment, the golf ball of the present invention includes a solid core, a boundary layer (preferably comprising a thermoplastic material), and a cover of polyurethane. Preferably all embodiments of the present invention include a cover made by casting the polyurethane cover over the core/boundary layer combination.

As is shown in FIG. 1, a first embodiment golf ball comprises a cover 14 over an inner core 12 and a boundary layer 13. The boundary layer 13 may be a single layer, as shown, or multiple layers. In this embodiment, the inner core 12 is preferably compression molded to yield a single layer solid core, the boundary layer 13 is preferably injection molded over the core, and the cover 14 is preferably cast over the boundary layer 13 and core 12 (which, preferably, has been pre-heated). The casting process is described below. As shown in FIG. 2, the golf ball has only a core 12 and a cover 14.

The solid core 12 of the golf ball is generally composed of a blend of a base rubber, a cross-linking agent, a free radical initiator, and one or more fillers or processing aids. A preferred base rubber is a polybutadiene having a cis-1,4 content of above about 90%, and more preferably 98% or above. Such materials are well known to those skilled in the art.

The use of cross-linking agents in a golf ball core is well known, and metal acrylate salts are examples of such cross-linking agents. For example, metal salt diacrylates, dimethacrylates, or mono(meth)acrylates are preferred for use in the golf ball cores of the present invention, and zinc diacrylate is a particularly preferred cross-linking agent. A commercially available suitable zinc diacrylate is SR-416 available from Sartomer Co., Inc., Exton, Pa. Other metal salt di- or mono- (meth)acrylates suitable for use in the present invention include those in which the metal is calcium or magnesium. In the manufacturing process it may be beneficial to pre-mix some cross-linking agent(s), such as, e.g., zinc diacrylate, with the polybutadiene in a master batch prior to blending with other core components.

Free radical initiators are used to promote cross-linking of the base rubber and the cross-linking agent. Suitable free radical initiators for use in the golf ball core 12 of the present invention include peroxides such as dicumyl peroxide, bis-(t-butyl peroxy) diisopropyl benzene, t-butyl perbenzoate, di-t-butyl peroxide, 2,5-dimethyl-2,5-di-5-butylperoxy-hexane, 1,1-di (t-butylperoxy) 3,3,5-trimethyl cyclohexane, and the like, all of which are readily commercially available.

Zinc oxide is also preferably included in the core formulation. Zinc oxide may primarily be used as a weight adjusting filler, and is also believed to participate in the cross-linking of the other components of the core (e.g. as a coagent). Additional processing aids such as dispersants and activators may optionally be included. In particular, zinc stearate may be added as a processing aid (e.g. as an activator). Any of a number of specific gravity adjusting fillers may be included to obtain a preferred total weight of the core 12. Examples of such fillers include tungsten and barium sulfate. All such processing aids and fillers are readily commercially available. The present inventors have found a particularly useful tungsten filler is WP102 Tungsten (having a 3 micron particle size) available from Atlantic Equipment Engineers (a division of Micron Metals, Inc.), Bergenfield, N.J.

Table 1 below provides the ranges of materials included in the preferred core formulations of the present invention.

TABLE 1

Core Formulations		
Component	Preferred Range	Most Preferred Range
Polybutadiene	100 parts	100 parts
Zinc diacrylate	20–35 phr	25–30 phr
Zinc oxide	0–50 phr	5–15 phr
Zinc stearate	0–15 phr	1–10 phr
Peroxide	0.2–2.5 phr	0.5–1.5 phr
Filler (e.g. tungsten)	As desired (e.g. 2–10 phr)	As desired (e.g. 2–10 phr)

In the present invention, the core components are mixed and compression molded in a conventional manner known to those skilled in the art. In a preferred form, the finished core 12 has a diameter of about 1.35 to about 1.64 inches for a golf ball 10 having an outer diameter of 1.68 inches. The core weight is preferably maintained in the range of about 32 to about 40 g. The core PGA compression is preferably maintained in the range of about 50 to 90, and most preferably about 55 to 80.

As used herein, the term "PGA compression" is defined as follows:

PGA compression value=180−Riehle compression value

The Riehle compression value is the amount of deformation of a golf ball in inches under a static load of 200 pounds, multiplied by 1000. Accordingly, for a deformation of 0.095 inches under a load of 200 pounds, the Riehle compression value is 95 and the PGA compression value is 85. While the inventors are aware of formulae contained in U.S. Pat. No. 5,368,304 and U.S. Pat. No. 5,813,923 that state that "PGA compression values=160−Riehle compression value", the inventors have adopted the alternative formula and definition set forth above.

Table 2 sets forth physical data for cores 12 that were manufactured according to the above-descriptionand incorporated into specific embodiments of golf balls 10 of the present invention. Each specific embodiment golf ball 10 is referred to and identified by the same ball example number throughout this specification.

TABLE 2

Core Properties			
Ball Ex. No.	Size (inches)	Specific Gravity	Compression (PGA)
1	1.500	1.139	68
2	1.505	1.142	70
3	1.520	1.142	70
4	1.530	1.142	70
5	1.494	1.157	70
6	1.510	1.157	68
7	1.489	1.157	60
8	1.510	1.155	70
9	1.510	1.155	60

As is described above, the present invention preferably includes at least one boundary layer 13 that preferably is composed of a thermoplastic (e.g. thermoplastic or thermoplastic elastomer) or a blend of thermoplastics (e.g. metal containing, non-metal containing or both). However, the golf ball 10 may have several boundary layers 13 disposed between the core 12 and the cover 14. Most preferably the

boundary layer 13 is composed of at least one thermoplastic that contains organic chain molecules and metal ions. The metal ion may be, for example, sodium, zinc, magnesium, lithium, potassium, cesium, or any polar metal ion that serves as a reversible cross-linking site and results in high levels of resilience and impact resistance. Suitable commercially available thermoplastics are ionomers based on ethylene copolymers and containing carboxylic acid groups with metal ions such as described above. The acid levels in such suitable ionomers may be neutralized to control resiliency, impact resistance and other like properties. In addition, other fillers with ionomer carriers may be used to modify (e.g. preferably increase) the specific gravity of the thermoplastic blend to control the moment of inertia and other like properties. Exemplary commercially available thermoplastic materials suitable for use in a boundary layer 13 of a golf ball of the present invention include, for example, the following materials and/or blends of the following materials: HYTREL® and/or HYLENE® products from DuPont, Wilmington, Del., PEBEX® products from Elf Atochem, Philadelphia, Pa., SURLYN® products from DuPont, and/or ESCOR® or IOTEK® products from Exxon Chemical, Houston, Tex.

The Shore D hardness of the boundary layer 13 should be about 65 or less. It is preferred that the boundary layer 13 have a hardness of between about 50–65 Shore D. In a preferred embodiment, the boundary layer 13 has a Shore D hardness in the range of about 52–65. One reason for preferring a boundary layer 13 with a Shore D hardness of 65 or lower is to improve the feel of the resultant golf ball. It is also preferred that the boundary layer 13 is composed of a blend of SURLYN® ionomer resins. Table 3 below sets forth physical data for suitable boundary layers 13 that were manufactured and incorporated into specific embodiments of golf balls 10 of the present invention. As is shown in Table 3 below, a boundary layer 13 with a lower Shore D hardness tends to have a lower flexural modulus as well.

and is available from Americhem, Inc., Cuyahoga Falls, Ohio, under the trade designation 38534X1. The specific gravity for each of the boundary layers 13 in Table 3 was 1.007. The flexural modulus provided in Table 3 was determined according to ASTM D790. The Shore D hardness provided in Table 3 was determined according to ASTM D2240.

In the preferred embodiment, the cover 14 of the golf ball 10 of the present invention is composed of a PPDI-based polyurethane system. Although the monomer has a tendency to sublime, thereby making it difficult to handle, the monomer has two isocyanate groups that exhibit widely different reactivities and make it particularly effective at providing polyurethane prepolymers with low content of free PPDI (in the range of 0.1 percent).

As mentioned previously, the polyurethane utilized in the present invention is composed of a PPDI-based prepolymer reacted with a curing agent. The PPDI-based prepolymer is formed from PPDI and a polyol such as an ester polyol, a polyether polyol, or a blend thereof. A preferred polyol is polycaprolactone. The curing agent, or curative, is a diol (e.g., 1,4 butane diol, trimethylpropanol), a mixture of diols (e.g., 1,4 butane diol and ethylene glycol, or other suitable glycols), a hydroquinone, a mixture of hydroquinones, a triol, a mixture of triols, a diamine, a mixture of diamines, an oligomeric diamine, a triamine, or a blend of some or all of these materials. Specifically, the cover 14 of the golf ball 10 of the present invention is most preferably composed of a polyurethane formed from a PPDI-based prepolymer and cured with a mixture of diols, such as, for example, a blend of 1,4 butane diol and glycols. Such a suitable blend of diol and glycols is available from Uniroyal Chemical Company, Inc. Middlebury, Conn., under the name as VIBRACURE® A250 has an equivalent weight of about 45. Other agents which may be utilized during the curing process include trimethyl glycol di-p-aminobenzoate (such as VERSALINK® 740M available from Air Products and

TABLE 3

Boundary Layer Properties

Ball	SURLYN ®			Barytes	Thickness	FlexMod	Shore D
Ex. No.	%8150	%9150	%6320	(phr)	(inches)	(psi)	Hardness
1	40	40	20	8	0.065	55100	58
2	50	50	0	9	0.050	78600	61
3	50	50	0	9	0.050	78600	61
4	50	50	0	9	0.050	78600	61
5	32	32	36	9	0.058	41400	55
6	37.5	37.5	25	9	0.058	51200	57
7	40	40	20	9	0.058	55109	58
8	50	50	0	9	0.055	78600	61
9	47.5	47.5	5	9	0.050	71300	61

SURLYN® 8150, 9150, and 6320 are, respectively, an ionomer resin composed of a sodium neutralized ethylene/methacrylic acid, an ionomer resin composed of a zinc neutralized ethylene/methacrylic acid, and an ionomer resin composed of a terpolymer of ethylene, methacrylic acid and n-butyl acrylate partially neutralized with magnesium, all of which are all available from DuPont, Polymer Products, Wilmington, Del.

As is indicated in Table 3, all of the boundary layers 13 in the examples include a predetermined amount of a baryte mixture. The baryte mixture is included as 8 or 9 parts per hundred parts of the ionomer resins. One preferred baryte mixture is composed of 80% barytes and 20% of an ionomer,

Chemicals, Inc., Allentown, Pa.); toluene ethylene diamine (such as ETHACURE® 100 available from Albemarle Corp., Baton Rouge, La.); cyclohexane dimethanol (readily available); hydroquinone-bis-hydroxyethyl ether (readily available); phenyldiethanol amine mixture (such as VIBRACURE ® A931 available from Uniroyal Chemical Co., Middlebury, Conn.); methylene dianiline sodium chloride complex (such as CAYTOR® 31 available from Uniroyal Chemical Co.); and/or prionene amine (readily available). This list of preferred agents (including chain extenders, cross-linkers and curing agents) is not meant to be exhaustive, as any suitable (preferably polyfunctional) chain extender, cross-linker, or curing agent may be used.

The cover 14 of the golf ball 10 of the present invention is preferably a castable thermoset polyurethane elastomer. For such a thermoset polyurethane elastomer, a PPDI-based prepolymer is preferably cured with at least one diol curative. Such a diol curative includes 1,4-butane diol, trimethylpropanol, or a mixture of diols (such as 1,4-butane diol and glycol, or other suitable glycols), a hydroquinone or mixture of hydroquinones, a triol or mixture of triols, or at least one of a diamine type curative(s), such as, methylenebis(ortho-chloroaniline), or ETHACURE® 300 or ETHACURE® 100 available from Albemarle Corp., or an oligomeric diamine, or a mixture of some or all of these materials, and most preferably using a mixture of 1,4-butane diol and glycols such as is available from Uniroyal Chemical Company, Inc., under the name VIBRACURE® A250.

The weight ratio of the PPDI-based prepolymer to the curative is preferably in the range of about 10:1 to about 30:1. Prior to curing, the PPDI-based prepolymer and curative are preferably stored separately. The PPDI-based polyurethane is formed by first heating and mixing the PPDI-based prepolymer with the curative in a mold, and then curing the mixture by applying heat and pressure for a predetermined time period. Additionally, a catalyst (e.g. dibutyl tin dilaurate, a tertiary amine, etc.) may be added to the mixture to expedite the casting process. Specific suitable catalysts include TEDA dissolved in di propylene glycol (such as TEDA L33 available from Witco Corp. Greenwich, Conn., and DABCO 33 LV available from Air Products and Chemicals Inc.,) which may be added in amounts of 2–5%, and more preferably TEDA dissolved in 1,4-butane diol which may be added in amounts of 2–5%. Another suitable catalyst includes a blend of 0.5% 33LV or TEDA L33 (above) with 0.1% dibutyl tin dilaurate (available from Witco Corp. or Air Products and Chemicals, Inc.) which is added to a curative such as VIBRACURE® A250. Furthermore, additives such as colorants may also be added to the mixture.

Although the golf ball cover 14 of the present invention is preferably manufactured in a casting process, the cover material may alternatively be provided as a thermoplastic polyurethane for injection molding of the cover 14 over the boundary layer 13 and/or core 12. For a thermoplastic polyurethane, the PPDI-based prepolymer is formed by reacting a polyol with PPDI. The PPDI-based prepolymer is then reacted with a chain extender, such as, for example, a diol or mixture of diols, a triol or mixture of triols, a diamine or mixture of diamines, etc. The resulting product is modified using conventional procedures to form a desired thermoplastic material for injection molding of the cover 14 over the boundary layer 13 and/or core 12.

The PPDI-based polyurethane cover 14 of the present invention exhibits good tensile strength, tear properties, and flexural modulus at lower hardnesses. In addition, because the preferred material is PPDI-based, the cover 14 has a tan δ value lower than conventional (e.g. MDI- and TDI-based) thermoplastics and thermoset urethanes. Thus, the PPDI-based polyurethane cover 14 of the present invention loses less energy as heat upon a high distortion or impact event (i.e. hysteresis) compared to these other polyurethane materials. It is believed that the relative superior mechanical and physical properties of the PPDI-based polyurethane cover 14 of the present invention is due to both the rigid rod-like structure of PPDI and the distribution of that structure throughout the polyurethane.

In the preferred embodiment, the PPDI-based prepolymer is preferably a PPDI reacted with a polycaprolactone. The PPDI-based prepolymer material is preferably degassed and

warmed in a first holding container prior to processing of the cover 14. The processing temperature for the PPDI-based prepolymer is preferably in the range of about 100–220° F., and most preferably in the range of about 120–200° F. The PPDI-based prepolymer is preferably flowable from the first holding container to a mixing chamber in a range of about 200–1100 grams of material per minute, or as needed for processing. In addition, the PPDI-based prepolymer material may be agitated in the first holding container, in the range of 0–250 rpm, to maintain a more even distribution of material and to eliminate crystallization.

In the preferred embodiment, the curative is a blend of 1,4 butane diol and glycol such as VIBRACURE® A250. As previously mentioned, other curatives may also be utilized in forming the cover 14 of the golf ball of the present invention. The curative is preferably degassed and warmed in a second holding container prior to processing of the cover 14. The processing temperature for the curative is preferably in the range of about 50–230° F., and most preferably in the range of about 80–200° F. The curative is preferably flowable from is the second holding container to the mixing chamber in the range of about 15–75 grams of material per minute, or as needed. If a catalyst is used for processing the cover 14, then the catalyst is added to the curative in the second holding container to form a curative mixture. Suitable catalyst are described above. The curative and catalyst are agitated, in the range of about 0 to 250 rpm, to maintain an even distribution of catalyst in the curative in the second holding container. It is preferred that catalyst is added in an amount in the range of about 0.25–5% by weight of the combined PPDI-based prepolymer and curative. Additives may be added to the curative as desired. It was discovered that hydrolytic instability of the polyurethane polymer may be avoided by the addition of a stabilizer such as STABOXYL® (available from Rheinchemie, Trenton, New Jersey), in amounts of about 0.25–5% of the polyurethane.

The PPDI-based prepolymer and curative mixture are preferably added to the common mixing chamber at a temperature in the range of about 160–220° F. A colorant material, such as, for example, titanium dioxide, barium sulfate, and/or zinc oxide in a glycol or castor oil carrier, and/or other additive material(s) as are well known in the art, may be added to the common mixing chamber. The amount of colorant material added is preferably in the range of about 0–10% by weight of the combined PPDI-based prepolymer and curative materials, and more preferably in the range of about 2–8%. Other additives, such as, for example, polymer fillers, metallic fillers, and/or organic and inorganic fillers (e.g. polymers, balata, ionomers, etc.) may be added as well to increase the specific gravity of the PPDI-based polyurethane cover 14 of the present invention. It was discovered that the addition of barytes (barium sulfate) or a blend of barytes and titanium dioxide (preferably added in a carrier glycol and/or castor oil) to the mixture, in the amounts of about 0.01–30%, may add sufficient weight to the PPDI-based polyurethane cover 14. The added weight to the cover 14 allows for a lower specific gravity for the core 12 thereby allowing for an increased resiliency of the core 12. The entire mixture is preferably agitated in the mixing chamber in the range of about 1 to 250 rpm prior to molding.

The resulting PPDI-based polyurethane cover material has the physical properties as listed in Table 4 below. Table 4 illustrates the exemplary properties of the cover 14 of the present invention as compared to prior cover materials.

TABLE 4

Typical Approximate Values			
Property	Present Invention	Prior Polyurethanes (MDI and TDI)	Ionomers
Shore D Hardness	45–60	50–60	45–75
Tensile Strength psi	6500–7900	3500–4000	2000–3500
Bashore Resilience	55–65%	45–55%	50–60%

As can be seen by comparing the data in Table 4, the cover **14** of the present invention exhibits hardness and resilience comparable to prior materials, however the cover material exhibits a much higher tensile strength than the prior materials.

The cover **14** of the present invention preferably has a thickness of between about 0.02–0.09 inches, or more preferably between about 0.02–0.065 inches, and most preferably between about 0.02–0.04 inches. Table below sets forth physical data for exemplary covers **14** of the present invention that were manufactured and incorporated into specific embodiments of golf balls **10** of the present invention.

TABLE 5

Cover Properties						
Ball Ex. No	Adiprene ® Prepolymer	Thickness inches	Tensile Strength	Specific Gravity	Bashore Resilience	Hardness Shore D
1	LFPX2950	0.0265	6500 psi	1.142	62–65%	47D
2	LFPX1951	0.0380	7900 psi	1.220	54–57%	53D
3	LFPX1951	0.0300	7900 psi	1.220	54–57%	53D
4	LFPX1951	0.0251	7900 psi	1.220	54–57%	53D
5	LFPX2950	0.0345	6500 psi	1.142	62–65%	47D
6	LFPX2950	0.0270	6500 psi	1.142	62–65%	47D
7	LFPX2950	0.0380	6500 psi	1.142	62–65%	47D
8	LFPX2950	0.0295	6500 psi	1.142	62–65%	47D
9	LFPX2950	0.0348	6500 psi	1.142	62–65%	47D

The prepolymers indicated in Table 5 are ADIPRENE® LFPX2950 and ADIPRENE® LFPX1951, which are available from Uniroyal Chemical Company. ADIPRENE® LFPX2950 and LFPX 1951 are both described by Uniroyal Chemical Company as PPDI-terminated polycaprolactone prepolymers. In the examples listed in Table 5, the PPDI-based prepolymer was cured with a 1,4-butane diol mixture (i.e. VIBRACURE® A250 from Uniroyal). The catalyst used was TEDA L33 from Witco Corp. Three percent TEDA L33 was added to the curative for mixing with LFPX2950, and two percent TEDA L33 was added the curative for mixing with LFPX1951. It is believed that blending 0.5% TEDA L33 with 0.1% dibutyl tin dilaurate is a beneficial catalyst for use with LFPX2950 (i.e. where the catalyst blend is added to the curative, e.g. A250).

As is mentioned above, the PPDI-based polyurethane is well suited to be used as a golf ball cover. Particularly, the PPDI-based polyurethane exhibits such good durability that a cover made from the material can be quite thin as compared to golf ball covers made from prior materials. For example, golf balls having covers made from the material of

the present invention having thicknesses of between about 0.02–0.04 inches performed well in durability test, as described below. Conventional thermoset polyurethane or polyurea golf ball covers sufficiently durable for use in competitive play (e.g. made from a polyurethane prepolymer, such as MDI, cured with a polyamine and 5–95% by weight of a difunctional glycol, see, Wu, U.S. Pat. No. 5,334,673) have a typical minimum cover thickness of at least twice this range (i.e. at least about 0.04–0.06–0.08 inches).

For example, it is believed that both the Titleist PROFESSIONAL™ and the Maxfli REVOLUTION® golf balls are wound golf balls having conventional polyurethane covers. Several Titleist PROFESSIONAL™ and the Maxfli REVOLUTION® golf balls were tested for durability and cut/shear. Several Titleist DT 2-Piece® golf balls (which is believed to have a polybutadiene core and a lithium ionomer cover that is 0.065" thick) and Precept EV® Extra Spin golf balls (which is believed to have a polybutadiene core and a ionomer cover that is 0.086" thick) were subjected to the same tests. In addition, several golf balls of the present invention, each having a core **12**, boundary layer **13** and cover **14** as described above, were also subjected to the same tests, and were found to substantially meet or exceed the median ball failure durability of the other balls.

Specifically, to test ball failure durability six balls of each kind were tested by firing each from an air cannon at a velocity of about 200 feet per second into a ball failure/durability testing box. After being shot, each ball was examined for "failure" (i.e. breakage or out of round). The test was repeated for each ball until it either failed or was fired 99 times. Table 6 below sets forth the ball failure durability data for the tested balls. In addition, cover cut and shear were tested on each ball by simulating a hard hit from a pitching wedge (by dropping a weight on an immobilized ball, perpendicular to the ball surface for cut and at a tangent to the ball surface for shear) and rating any damage on a scale ranging from 1.0 (poor rating, severe damage) to 5.0 (excellent rating, little or no damage). The cover cut and shear testing results are also shown in Table 6.

TABLE 6

Durability and Cut/Shear Testing Data

Ball Tested	Cover Material	Cover Thickness	Cut/ Shear	Durability (shots) Min.	Max.	Median
Titleist Professional ™	Conventional polyurethane	0.065"	2.0/4.0	20	38	30
Maxfli Revolution ®	Conventional polyurethane	0.050"	3.5/5.0	15	24	19.5
Titleist DT ®	lithium ionomer	0.065"	3.5/1.0	32	58	42
Precept EV ®	Ionomer	0.086"	3.0/3.5	28	161*	135*
Ex. No. 1	present PPDI-polyurethane	0.0265	3.0/3.0	29	61	59
Ex. No. 2	present PPDI-polyurethane	0.0380	3.0/2.5	63	99	80
Ex. No. 3	present PPDI-polyurethane	0.0300	3.0/3.0	47	98	98
Ex. No. 4	present PPDI-polyurethane	0.0251	3.0/3.0	69	99	98
Ex. No. 5	present PPDI-polyurethane	0.0345	2.5/3.0	12	26	20
Ex. No. 6	present PPDI-polyurethane	0.0270	3.0/3.0	19	57	43
Ex. No. 7	present PPDI-polyurethane	0.0380	4.0/3.0	51	69	60
Ex. No. 8	present PPDI-polyurethane	0.0295	3.5/3.0	14	65	41
Ex. No. 9	present PPDI-polyurethane	0.0348	3.0/3.5	n/a	n/a	n/a

*The Precept EV balls were tested prior to limiting the maximum number to 99.

The data in Table 6 shows that golf balls **10** having a PPDI-polyurethane cover **14** of the present invention are substantially as cut resistant and nearly as shear resistant and as durable as golf balls having much thicker covers whether those covers are made from ionomers or prior polyurethane materials.

For comparison purposes, several test balls were prepared having cores and boundary layers pursuant to the present invention, but having covers composed of a MDI-based polyurethanes. These MDI example balls each had a core formulated as described above and measuring 1.550 inches. The MDI example balls each had a boundary layer comprising a 1:1 mixture of Surlyn® 8150 and Surlyn® 9150, and having thicknesses as described in Table 6A below. The MDI-based polyurethanes used for the covers of these MDI example balls were prepared by reacting VIBRATHANE® 997 or a 1:1 mixture of VIBRATHANE® 997 and VIBRATHANE® 670 with 1,4-butanediol. VIBRATHANE® 997 and VIBRATHANE® 670 are readily available from Uniroyal Chemical Co. The covers had thicknesses as described in Table 6A below. The MDI example balls were tested for cover shear resistance pursuant to the shear testing procedure described above. The testing results for the MDI example balls are reported in Table 6A.

TABLE 6A

MDI Example Balls Properties and Cover Shear Data

MDI Example Ball No.	Boundary Thickness (inches)	Vibrathane ® Cover Material	Cover Thickness (inches)	Cover Shear
MDI Ex. 1	0.035	997	0.0300	1.0–1.5
MDI Ex. 2	0.045	997	0.0200	1.5
MDI Ex. 3	0.045	997:670 (1:1)	0.0200	1.0
MDI Ex. 4	0.035	997:670 (1:1)	0.0300	1.5–3.0

TABLE 6A-continued

MDI Example Balls Properties and Cover Shear Data

MDI Example Ball No.	Boundary Thickness (inches)	Vibrathane ® Cover Material	Cover Thickness (inches)	Cover Shear
MDI Ex. 5	0.035	997	0.0300	1.0–1.5
MDI Ex. 6	0.045	997	0.0200	1.5
MDI Ex. 7	0.045	997:670 (1:1)	0.0200	1.0

As is shown by comparing the data in the above tables, particularly Tables 6 and 6A, the golf balls **10** of the present invention are much more shear resistant than the MDI example golf balls having covers comprising typical prior MDI-based polyurethane systems.

The diameter of the core **12** and the thickness of the boundary layer **13** and cover **14** of the present invention are dependent on the desired diameter of the golf ball **10**. The inner core **12** preferably has a diameter in the range of about 1.35 to 1.70 inches and the boundary layer **13** preferably has a wall thickness in the range of about 0.02 to 0.09 inches. If the desired diameter of the golf ball **10** is about 1.68 inches, then more preferably the core **12** has a diameter in the range of about 1.40 to 1.65 inches and the boundary layer **13** has a wall thickness in the range of about 0.02 to 0.075 inches, and most preferably the core **12** has a diameter in the range of about 1.45 to 1.60 inches and the boundary layer **13** has a wall thickness in the range of about 0.02 to 0.067 inches. If the desired diameter of the golf ball **10** is about 1.8 inches, then more preferably the core **12** has a diameter in the range of about 1.55 to 1.72 inches and the boundary layer **13** has a wall thickness in the range of about 0.02 to 0.09 inches, and most preferably the core **12** has a diameter in the range of about 1.6 to 1.72 inches and the boundary layer **13** has a wall thickness in the range of about 0.02 to 0.06 inches.

In manufacturing the golf ball **10** of the present invention, the boundary layer **13** is preferably injection molded about

the inner core 12 in a conventional manner, resulting in a golf ball precursor product composed of a combination of an inner core 12 and a boundary 13. Alternatively, the golf ball precursor product may only be the core 12. Depending on the desired diameter of the golf ball 10, the inner core 12 and the boundary layer 13 combination preferably has an overall diameter in the range of about 1.46 to 1.76 inches. If the desired diameter of the golf ball 10 is about 1.68 inches, then the core 12 and boundary layer 13 combination more preferably has an overall diameter in the range of about 1.55 to 1.64 inches, and most preferably in the range of about 1.6 to 1.64 inches. If the desired diameter of the golf ball 10 is about 1.8 inches, then the core 12 and boundary layer 13 combination more preferably has an overall diameter in the range of about 1.64 to 1.67 inches, and most preferably in the range of about 1.72 to 1.76 inches.

In the preferred manufacturing process, the PPDI-based polyurethane cover material (i.e. the mixture composed of the PPDI-based prepolymer, curative with catalyst, and any additives, such as colorant, etc.) is preferably introduced into a first mold cavity of a mold cavity pair at T0. About 30–90 seconds later (i.e. T0+30–90 seconds or T1) the golf ball precursor product (preferably including a boundary layer 13), which preferably has been preheated as described in detail below, is then held (e.g. via suction equipment) contacting the cover material in the first mold cavity in what will be the spherical center of the mold cavity pair. The cover material is allowed to at least partially cure (typically between about 10–30 seconds, i.e., until about T1+10–30 seconds, i.e. T2), and then the core is released. Concurrently, the cover material is preferably introduced into a second cavity of the mold cavity pair at a time which enables it to set for about 30–90 seconds prior to T2, and then the mold is closed (thereby mating the first mold cavity to the second mold cavity), and subjected to heat and pressure to cure the cover material for about 2–10 minutes at about 140–220° F. and a pressure of about ⅓–2 ton per cavity in the mold thereby forming a cover 14 on the golf ball precursor product. The covered balls are then removed from the mold, allowed to cool, and preferably post-cured at about 140–250° F. for about 4–8 hours.

As is mentioned above, the golf ball precursor product, core or core and boundary layer combination, is preferably preheated prior the casting process. The preheating process is described in detail in co-pending patent application Ser. No. 09,296,197 entitled "Golf Balls and Methods of Manufacturing the Same", which has been assigned to the assignee of the present invention, and which is hereby incorporated by reference as if fully set forth herein. However, the present invention is not limited to the techniques disclosed in this co-pending application.

As is described in the co-pending application, the pre-heating step is preferably accomplished by applying heat to the core and any boundary layers, preferably to cause the core and any boundary layers to undergo thermal expansion. It should be appreciated that while the pre-heating step is described as being after core formation, the present methods also contemplate heating the core both during and after the formation of the golf ball core. In this manner, some of the heat that may be present or liberated in the core from the core formation process may be used in the pre-heating step. By undergoing thermal expansion, the volume of the ball increases from its initial size. Preferably, the core and any intermediate boundary layer is heated, prior to applying the cover, to a temperature of about 135° F. to about 175° F., and more preferably between about 140° F. to about 160° F. This pre-heating preferably occurs for about one hour, or for such time as needed to achieve an amount of thermal expansion prior to cover formation such that the cover will not crack, and/or to achieve a desired improvement in cover molding cycle time, as described below. Although the duration of the pre-heating step is not believed to be critical, this preferred amount of time permits substantially even heating of the core and any intermediate boundary layer and results in substantially steady-state thermal conditions within the core and any intermediate boundary layer.

While the temperature ranges and heating times disclosed above are the preferred ranges and times, it should be noted that the invention is not limited to any exact temperature or heating time. The purpose of the pre-heating step is to subject the core and any intermediate boundary layer to an increase in temperature to cause volumetric thermal expansion. This expansion can occur within any number of absolute temperatures over any period of heating time that fall within the operability range of the materials used. For example, any temperature differential and heating time that causes a sufficient amount of thermal expansion of the core and optional boundary layer can be used. The amount of thermal expansion preferred will vary depending on, at least, the cover material(s) and cover thickness to be used for manufacturing the golf ball 10. For example, for a relatively rigid cover material or a relatively thin cover, it is preferable to cause a relatively larger amount of thermal expansion to the core 12 and optional boundary layer 13 to substantially prevent cover cracking.

The Volumetric thermal expansion of the core 12 and optional boundary layer 13 may be expressed as a percentage, as follows:

$$\left[\frac{(Vol_{final} - Vol_{initial})}{Vol_{initial}} \times 100\right] \%$$

where Vol_{final} is the average volume of the core 12 or the core 12 and one or more optional boundary layers 13 at the high temperature, and $Vol_{initial}$ is the average volume of the core 12 or the core 12 and one or more optional boundary layers 13 at the lower, initial starting temperature. It has been found that a volumetric expansion of at least about 1.2% is substantially sufficient to prevent cover cracking when using a thermoset polyurethane cover material in a casting process. It will be understood, however, that this is not intended to serve as a lower limit for the volumetric thermal expansion. Instead, the lower limit for a given system will depend on the materials, the golf ball construction, and the molding processes used in the system. Determination of this limit for a given system is within the level of skill of those skilled in the art.

After pre-heating the core 12, or the core 12 and one or more optional boundary layers 13, the cover 14 is applied. The cover 14 is preferably applied while the core 12 and optional boundary layers 13 are at an increased temperature, and most preferably at the increased temperature obtained during the pre-heating step.

The present invention provides a very durable cover 14 having an excellent sound and feel, and as such enables designing golf balls having a maximized core size. Maximizing core size typically provides maximum golf ball COR and, therefore, maximum distance for a given golf club head speed. While sound and feel are subjective observations of a golfer, it was attempted to quantify the feel of golf balls 10 of the present invention. About three exemplary golf balls 10 of the present invention (as described in the examples herein) and about three Bridgestone Precept EV® Extra Spin golf balls were provided to various professional golfers

and testers who performed side-by-side comparisons both on a fairway (using irons and drivers) and on and around a green (chips and putts). After and while comparing the balls the testers were asked their opinion regarding the feel of the balls (i.e. better or worse than the Precept EV® (Extra Spin golf ball). The Precept EV®) Extra Spin golf ball was chosen for this test even though it has an ionomer cover because it is commonly considered to be a golf ball having a good balance between feel, distance, control, and durability. While it should be understood that the feel of a golf ball is a very subjective observation, a majority of the testers determined that the exemplary balls of the present invention described as examples herein had a feel that was better than the Precept EV® Extra Spin golf balls.

The COR of each ball was also tested. The COR was tested by shooting each ball from an air cannon at various speeds up to about 180 feet per second toward a large rigid mass (e.g. a wall), measuring the velocity of the ball going toward the large rigid mass and the velocity of the ball on rebound, and then calculating the ratio of the velocity of a ball rebound versus the velocity of the ball prior to hitting the wall at each of the various speeds tested. A curve was then graphed to fit the various calculated ratio points at the corresponding test speed, and then the COR was taken as that point at an intersection of the curve with a speed of 143.8 feet per second. The Precept EV® Extra Spin ball was tested as having a COR of 77.4, the Titleist DT® ball had a COR of 78.8, the Titleist PROFESSIONAL™ ball had a COR of 77.2, and the Maxfli REVOLUTION® ball had a COR of 77.1. As is shown in Table 7 below, the exemplary golf balls of the present invention all have superior or substantially similar CORs to those presently available.

TABLE 7

COR Data

Golf Ball	COR
Precept EV ® Extra Spin	77.4
Titleist DT ®	78.8
Titleist Professional ™	77.2
Maxfli Revolution ®	77.1
Ex. No. 1	78.4
Ex. No. 2	78.2
Ex. No. 3	78.3
Ex. No. 4	78.5
Ex. No. 5	77.9
Ex. No. 6	78.8
Ex. No. 7	77.8
Ex. No. 8	79.4
Ex. No. 9	N/A

In addition, golf balls **10** of the present invention were analytically evaluated for distance performance. Generally, it is well understood by those skilled in the art that the distance a golf ball will travel may be predicted based on certain measured robot testing initial launch information (e.g. initial velocity, spin, launch angle, etc.) and certain aerodynamic properties (e.g. lift and drag characteristics during flight). Based on such analytical predictions the balls of the present invention were found to travel farther than prior balls.

Thus, the cover 14 of the preferred golf ball 10 of the present invention, exhibits enhanced feel both on the fairways and on the greens, and enables a ball having superior coefficients of restitution and farther predicted distance for a given set of initial launch conditions.

In summary, a golf ball 10 of the present invention has a cover **14** made from the PPDI-based polyurethane described above. As is described above, the overall thickness of the cover **14** of the present invention is preferably about 0.02 to 0.09 inches, more preferably about 0.02 to 0.065 inches, and most preferably about 0.02 to 0.04 inches. Thus, if the desired diameter of the golf ball **10** is about 1.68 inches, then the combination of the core **12** and boundary layer **13** preferably has an overall diameter in the range of about 1.50 to 1.64 inches, more preferably has an overall diameter in the range of about 1.55 to 1.64 inches, and most preferably has an overall diameter in the range of about 1.60 to 1.64 inches. This configuration enables use of a boundary layer **13** which is preferably stiff relative to the core **12** to give a resultant ball **10** a substantially similar or even higher COR as compared to conventional balls and, therefore, a comparatively further overall distance. In addition, the thin cover enables golf balls having large cores. It is well understood that increasing the core diameter of a golf ball generally translates into an improved feel with increased COR which in turn generally translates into an increased initial velocity and enhanced overall travel distance. Furthermore, use of a boundary layer **13** enables manipulation of the specific gravity of each layer to maximize the moment of inertia of the ball to lower spin rate to provide better playability and control, and optimized straightness, flatness, and length of driven golf ball.

It is preferred that a golf ball **10** of the present invention has a core **12**, a boundary layer **13** and a PPDI-based polyurethane cover **14**. The solid core **12** is composed of an elastomeric material having a diameter of between about 1.35–1.70 inches (depending on the desired final size of the ball), and a PGA compression of between about 50–80. The boundary layer **13** is composed of a thermoplastic (e.g. thermoplastic and/or thermoplastic elastomer) material having a hardness of between about 52–65 Shore D, a flexural modulus of between about 25,000–65,000 psi, and a wall thickness of between about 0.02–0.09 inches. The PPDI-based polyurethane cover **14** has a hardness of between about 45–60 Shore D, a flexural modulus of between about 12,000–35,000 psi, a Bashore resilience of between about 57–65, a tensile strength of between about 5900–7500 psi, and a wall thickness of between about 0.02–0.065 inches. While the cover **14** is described as preferably covering a solid core having a boundary layer, it could also be used on different cores such as wound, foam, hollow, or multilayered cores.

Exemplary golf balls **10** (examples numbered 1–9) embodying the above-described invention were prepared and tested according to the descriptions given above. The golf balls **10** were each constructed having a core **12** made from the materials and having the properties described in the text and Tables 1 and 2 above, a boundary layer **13** made from the materials and having the properties described in the text and Table 3 above, and a PPDI-based polyurethane cover **14** made from the materials and having the properties described in the text and Table 5 above. The finished balls were analyzed for their weight, PGA compression, and, as is reported in Table 7 above, COR. The results of these analyses are reported in Table 8 below.

TABLE 8

Miscellaneous Ball Data

Ball Ex. No.	Ave Diameter (inches)	Average Weight (g)	PGA Compression
1	1.6830	45.29	98
2	1.6811	45.66	98

TABLE 8-continued

Miscellaneous Ball Data

Ball Ex. No.	Ave Diameter (inches)	Average Weight (g)	PGA Compression
3	1.6800	45.57	98
4	1.6802	45.70	95
5	1.6790	45.68	89
6	1.6789	45.54	95
7	1.6809	45.66	87
8	1.6790	45.80	102
9	1.6797	45.63	89

Table 9 below compiles the data shown above for the nine exemplary balls of the present invention as described above.

TABLE 9

Compilation of Data

Property	Ball Ex. 1	Ball Ex. 2	Ball Ex. 3	Ball Ex. 4	Ball Ex. 5	Ball Ex. 6	Ball Ex. 7	Ball Ex. 8	Ball Ex. 9
Core									
Size (inches)	1.500	1.505	1.520	1.530	1.494	1.510	1.489	1.510	1.510
Specific Gravity	1.139	1.142	1.142	1.142	1.157	1.157	1.157	1.155	1.155
Compression*	68	70	70	70	70	68	60	70	60
Mantle Layer									
% Surlyn 8150	40	50	50	50	32	37.5	40	50	47.5
% Surlyn 9150	40	50	50	50	32	37.5	40	50	47.5
% Surlyn 6320	20	0	0	0	36	25	20	0	5
% Barytes	8	9	9	9	9	9	9	9	9
Thickness (inches)	0.065	0.050	0.050	0.050	0.058	0.058	0.058	0.055	0.050
Flexural Modulus**	55100	78600	78600	78600	41400	51200	55100	78600	71300
Specific Gravity	1.007	1.007	1.007	1.007	1.007	1.007	1.007	1.007	1.007
Hardness***	58	61	61	61	55	57	58	61	61
Cover									
Adiprene Prepolymer	LFPX 2950	LFPX 1951	LFPX 1951	LFPX 1951	LFPX 2950	LFPX 2950	LFPX 2950	LFPX 2950	LFPX 2950
Thickness (inches)	.0265	.0380	.0300	.0251	.0345	.0270	.0380	.0295	.0348
Tensile Strength (psi)	6500	7900	7900	7900	6500	6500	6500	6500	6500
Specific Gravity	1.142	1.220	1.220	1.220	1.142	1.142	1.142	1.142	1.142
Bayshore Rebound %	62–65	54–57	54–57	54–57	62–65	62–65	62–65	62–65	62–65
Flexural Modulus**	>10K	>10K	>10K	>10K	>10K	>10K	>10K	>10K	>10K
Hardness***	47	53	53	53	47	47	47	47	47
Overall Ball									
Cut	3.0	3.0	3.0	3.0	2.5	3.0	4.0	3.5	3.0
Shear	3.0	2.5	3.0	3.0	3.0	3.0	3.0	3.0	3.5
Durability:									
Maximum	61	99	98	99	26	57	69	65	n/a
Minimum	29	63	47	69	12	19	51	14	n/a
Median	59	80	98	98	20	43	60	41	n/a
COR 143.8 fps	78.4	78.2	78.3	78.5	77.9	78.8	77.8	79.4	n/a
Ave. Diameter (inches)	1.683	1.681	1.680	1.680	1.679	1.679	1.681	1.679	1.680
Ave. Weight (grams)	45.29	45.66	45.57	45.70	45.68	45.54	45.66	45.80	45.63
Ave. Compression*	98	98	98	95	89	95	87	102	89

*PGA compression;
**ASTM D790;
***Shore D, ASTM D2240;

While embodiments of the present invention have been shown and described, various modifications may be made without departing from the scope of the present invention, and all such modifications and equivalents are intended to be covered. For example, the size and thickness ranges given are primarily directed to a ball having a finished diameter of about 1.68 inches which would thereby comply with current regulations of the United States Golf Association. However, balls of different sizes are considered to be included within the scope of the present invention.

I claim as my invention the following:

1. A golf ball comprising:

a core; and

a thermoset polyurethane cover formed from reactants comprising a p-phenylene diisocyanate prepolymer and a mixture of diols.

2. The golf ball according to claim 1 further comprising at least one boundary layer disposed between the core and the thermoset polyurethane cover.

3. The golf ball according to claim 1 wherein the thermoset polyurethane cover has a tensile strength in the range of about 6500 to about 7900 psi.

4. The golf ball according to claim 1 wherein the p-phenylene diisocyanate prepolymer comprises p-phenylene diisocyanate and one or more polyester polyols, polyether polyols or a mixture thereof.

5. The golf ball according to claim 1 wherein the p-phenylene diisocyanate prepolymer comprises p-phenylene diisocyanate and a polycaprolactone polyol.

6. The golf ball according to claim 1 wherein the reactants forming the thermoset polyurethane cover further comprise at least one catalyst.

7. The golf ball according to claim 6 wherein the catalyst is a tertiary amine.

8. The golf ball according to claim 1 wherein the reactants forming the thermoset polyurethane cover further comprise

at least one colorant, filler, processing aid, stabilizer, or mixture thereof.

9. The golf ball according to claim **8** wherein the reactants forming the thermoset polyurethane cover further comprise at least one stabilizer that retards hydrolytic instability.

10. The golf ball according to claim **1** wherein the thermoset polyurethane cover has a hardness of between about 45–60 Shore D, a flexural modulus of between about 12,000–35,000 psi, a Bashore resilience of between about 57–65, and a tensile strength of between about 5900–7500 psi.

11. The golf ball according to claim **1** wherein the thermoset polyurethane cover has a thickness of less than about 0.04 inches.

12. A golf ball comprising:

a core;

a boundary layer encompassing the core, the boundary layer composed of a thermoplastic material; and

a PPDI-based thermoset polyurethane cover formed from components comprising a p-phenylene diisocyanate prepolymer and a mixture of diols.

13. The golf ball according to claims **12** wherein the boundary layer comprises at least one ionomer or a blend of ionomers.

14. The golf ball according to claim **12** wherein the boundary layer has a Shore D hardness less than 65.

15. The golf ball according to claim **12** wherein the core comprises polybutadiene rubber and tungsten.

16. The golf ball according to claim **12** wherein the core comprises at least one construction from the group consisting of solid, wound, foam, hollow and multi-layered.

17. The golf ball according to claim **12** wherein the core has a diameter of at least about 1.4 inches and the golf ball has a diameter of about 1.68 inches.

18. The golf ball according to claim **17** wherein the PPDI-based thermoset polyurethane cover has a thickness of no more than about 0.04 inches.

19. The golf ball according to claim **17** wherein the PPDI-based thermoset polyurethane cover has a thickness of no more than 0.03 inches.

20. The golf ball according to claim **12** wherein the components forming the PPDI-based thermoset polyurethane cover p-phenylene diisocyanate and one or more polyester polyols, polyether polyols or a mixture thereof.

21. The golf ball according to claim **12** wherein the boundary layer has a flexural modulus of 65,000 pounds per square inch or less.

22. The golf ball according to claim **12** wherein the PPDI-based thermoset polyurethane cover has a hardness of between about 45–60 Shore D, a flexural modulus of between about 12,000–35,000 psi, a Bashore resilience of between about 57–65, and a tensile strength of between about 5900–7500 psi.

* * * * *

EXHIBIT 23

US006458046B1

(12) **United States Patent**
Halko et al.

(10) **Patent No.: US 6,458,046 B1**
(45) **Date of Patent: *Oct. 1, 2002**

(54) **MULTI-LAYER, WOUND GOLF BALL**

(75) Inventors: **Roman D. Halko**, Natick; **Brian R. Fletcher**, New Bedford, both of MA (US)

(73) Assignee: **Acushnet Company**, Fairhaven, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **09/641,758**

(22) Filed: **Aug. 21, 2000**

(51) **Int. Cl.**[7] **A63B 37/06**; A63B 37/08; A63B 37/00

(52) **U.S. Cl.** **473/361**; 473/357; 473/351; 473/354

(58) **Field of Search** 473/356, 357, 473/361, 362, 363, 365, 378, 371, 373, 374, 376

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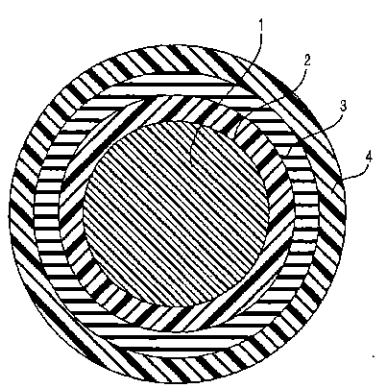
Primary Examiner—Paul T. Sewell
Assistant Examiner—Alvin A. Hunter
(74) *Attorney, Agent, or Firm*—Swidler Berlin Shereff Friedman, LLP

(57) **ABSTRACT**

A multi-layer golf ball can be prepared, possessing the performance characteristics of both a solid ball and a wound ball, by selecting the content and thickness of one or more of the layers, wherein the multi-layer golf ball comprises a center, an intermediate layer, a wound layer of tensioned material, and a cover, such that any one or more of the following are satisfied: (a) at least a portion of the intermediate layer includes a thermoset material; (b) the winding includes fiber, glass, carbon, polyether urea, polyether block copolymers, polyester urea, polyester block copolymers, isotactic-poly(propylene), polyethylene, polyamide, poly (oxymethylene), polyketone, poly(ethylene terephthalate), poly(p-phenylene terephthalamide), poly(acrylonitrile), diaminodicyclohexylmethane, dodecanedicarboxylic acid, or copolymers or combinations thereof; (c) the thickness of the wound layer is less than about 1 mm; and (d) at least a portion of the cover includes a thermoset material. Methods of preparation of such golf balls are also recited.

35 Claims, 1 Drawing Sheet



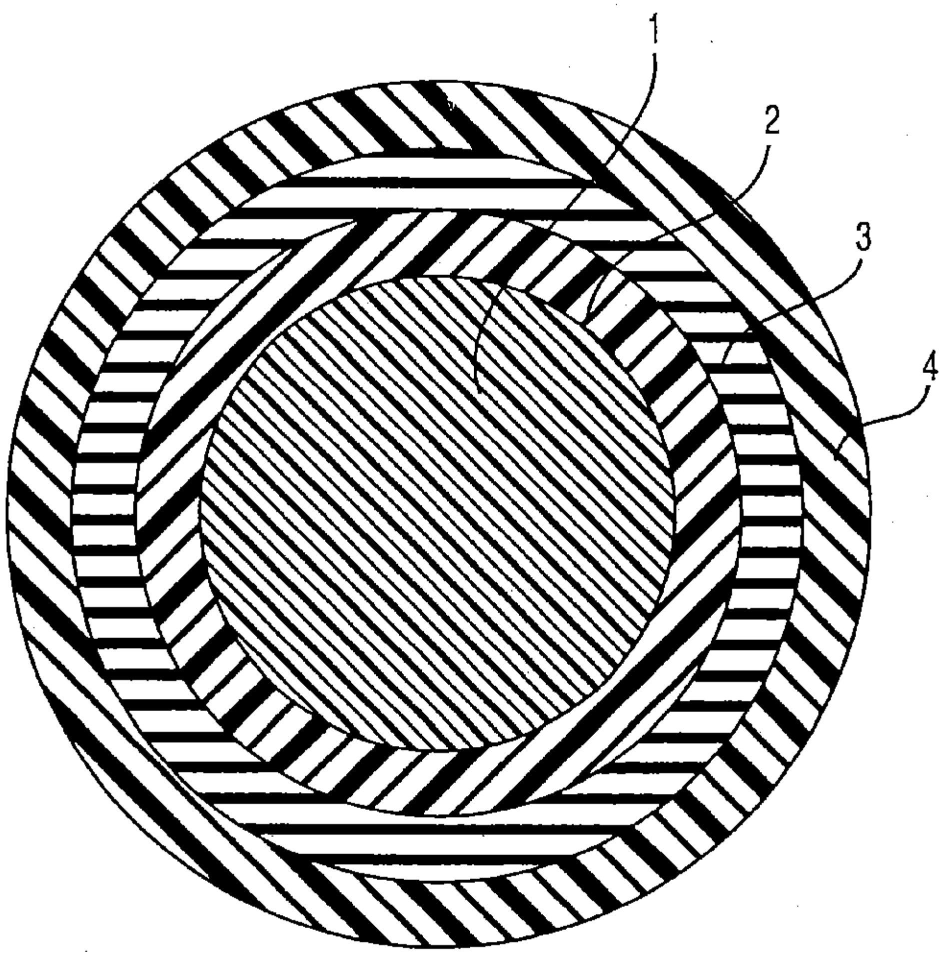


Fig. 1

MULTI-LAYER, WOUND GOLF BALL

FIELD OF THE INVENTION

The present invention is directed to a multi-layer, wound golf ball, especially one with the combined performance characteristics of both a wound and solid construction. In particular, the present invention relates to a golf ball with a wound thread layer disposed between the cover and a core, which comprises a center and an intermediate layer disposed about the center.

BACKGROUND OF THE INVENTION

Conventional golf balls can be divided into two general types or groups: solid balls and wound balls. The difference in play characteristics resulting from these different types of constructions can be quite significant.

Solid balls with a two-piece construction are generally most popular with the average recreational golfer, because they provide a very durable ball for a reasonable price while also providing maximum distance. Two piece solid balls are typically made with a single solid core, usually made of a crosslinked rubber, which is encased by a hard cover material. The combination of the core and cover materials, which are very rigid, provide a hard feel for the ball when it is struck with a club and provide a ball that is virtually indestructible by golfers. This combination of materials helps impart a high initial velocity to the ball, which results in improved distance. In addition, this combination provides balls having a relatively low spin rate, which tends to provide greater driver distance.

At the present time, however, the wound ball generally remains the preferred ball of more advanced players due to its spin and feel characteristics. Wound balls typically have either a solid rubber or fluid-filled center around which many yards of a tensioned elastic thread or yarn are wrapped to form a wound core. Typically, the tensioned elastic thread is made of synthetic polyisoprene or natural rubber. For example, U.S. Pat. Nos. 5,674,137; 5,716,293; 5,816,937; 5,816,940; 5,816,941; 5,816,942; 5,888,151; and 5,976,034 relate to multi-layer, wound golf balls containing rubber thread windings. The wound core is then typically covered with a durable cover material, such as a SURLYN® or a similar material, or a softer "performance" cover, such as balata or polyurethane.

Typically, a single strand of thread is employed in forming the wound core. This thread can be wrapped at variable tension as disclosed in U.S. Pat. No. 4,783,078. Some balls, however, have used two or more different threads of different dimensions to form the wound core. In this case, the innermost thread may be wound at a different tension and with a different pattern than the outermost thread. Furthermore, the outermost thread is generally wound in a more open pattern to form larger gaps between the thread, which helps ensure good amalgamation between the cover and the wound core.

The United States Golf Association (US GA) has instituted a rule that prohibits the competitive use in any USGA sanctioned event of a golf ball that can achieve greater than an initial velocity of 76.2 meters per second (m/s), or 250 ft/s, when tested in a standardized device operated by the USGA (referred to hereinafter as "the USGA test"). An allowed tolerance of 2 percent, however, permits manufacturers to produce golf balls that achieve an initial velocity of up to 77.7 m/s (255 ft/s).

Players generally seek a golf ball that delivers maximum distance off the tee, which requires a high initial velocity upon impact. Therefore, in an effort to meet the demands of the marketplace while providing conforming balls, manufacturers typically strive to produce golf balls with initial velocities no greater than that permitted by the USGA test. Manufacturers try to provide these balls with a range of different properties and characteristics, such as spin and compression, to enhance short iron shots, as well.

To meet the needs of golfers having varying levels of skill, golf ball manufacturers are also concerned with varying the compression of the ball, which is a measurement of the deformation of a golf ball under a load. A ball with a higher compression feels harder than a ball of lower compression. Wound golf balls generally have lower compression and spin characteristics that are preferred by better players. Whether wound or solid, all golf balls become generally more resilient (i.e., have higher initial velocities) as compression increases. Manufacturers of both wound and solid construction golf balls must balance the requirement of higher initial velocity from higher compression with the desire for a softer feel from lower compression.

Wound balls typically enable a skilled golfer to have more control over the ball's flight and final position using short-iron shots than many non-wound balls. Particularly with approach shots into the green, the typically higher spin rate of soft covered, wound balls enables many golfers to stop the ball very near its landing position. Soft covered wound balls with their lower compression, however, tend to exhibit a lower initial velocity than hard covered solid balls. This characteristic, in combination with a higher spin rate than solid balls, means wound balls generally display shorter distance than hard covered solid balls when struck with a driver. The advantages of wound constructions over solid ones, however, are more related to spin and controllability than distance.

A softer feel is the result of a lower compression, but feel is also affected by cover hardness and thickness. In wound constructions, a thinner cover will have a softer feel, so manufacturers often strive to produce balls with the thinnest possible covers. The packing density of the windings and the cover formulation process can affect the thickness of the cover, but other factors related to the cover will also affect this thickness.

It is known in the art to modify conventional solid balls by altering the typical single layer core and single cover layer construction to provide a multi-layer ball having such as a dual cover layer and/or a ball having a mantle layer disposed between the cover and the core. Like the solid cores, various cover layers and mantle layers are typically formed of polybutadiene that is chemically crosslinked with zinc diacrylate and/or similar crosslinking agents. The playing characteristics of multi-layer balls, for example compression, can be tailored by varying the properties of one or more of these mantle layers, also known as intermediate layers.

A number of patents are directed towards modifying the properties of layers used in forming conventional solid balls, multi-layer balls having two or more cover layers, dual core layers, such as those having a mantle layer disposed between the cover and center, and/or wound balls. For example, U.S. Pat. Nos. 5,674,137; 5,816,937; 5,816,942; and 5,885,172 are directed to multi-layer wound golf balls having multi-layer covers. For example, U.S. Pat. Nos. 3,147,324; 5,816,937; and 5,885,172 are directed to golf balls, or methods for making such, having a polyurethane outer cover. For example, U.S. Pat. Nos. 5,716,293 and 5,020,803 are directed to wound golf balls having a dual layer liquid core.

U.S. Pat. No. 5,020,803 to Gendreau et al. discloses a golf ball containing a liquid-filled center, surrounded by a heavy-walled sphere, around which a wound layer is disposed to form a wound core. The heavy-walled sphere is preferably rubber and is between 0.16 and 0.64 cm thick.

British Patent No. GB 2337706 A to Sumitomo Rubber Industries, Ltd. discloses a multilayer wound golf ball having a dual layer center, both layer being formed from the same materials. The diameter of both center layers are limited, as are the JIS-C hardnesses, and cover is made from a thermoplastic material.

Polyurethane is the product of a reaction between a polyurethane prepolymer and a curing agent. The polyurethane prepolymer is a product formed by a reaction between a polyol and a diisocyanate. The curing agents used previously are typically diamines or glycols. A catalyst is often employed to promote the reaction between the curing agent and the polyurethane prepolymer.

Polyurethanes are typically divided into two categories: thermosets and thermoplastics. Thermoplastic polyurethanes are typically formed by the reaction of a diisocyanate, such as 4,4'-diphenylmethane diisocyanate ("MDI") or 3,3'-dimethyl-4,4'-biphenylene diisocyanate ("TODI"), and a polyol cured with a diol, such as 1,4-butanediol. Thermoset polyurethanes are typically formed by the reaction of a diisocyanate, such as 2,4-toluene diisocyanate ("TDI") or methylene-bis-(4-cyclohexyl isocyanate) ("HMDI"), and a polyol which is cured with a polyamine, a triol such as trimethylol propane, or a tetrafunctional glycol, such as N,N,N', N'-tetra-bis-(2-hydroxypropyl) ethylenediamine.

U.S. Pat. No. 4,123,061 teaches a golf ball made from a polyurethane prepolymer of polyether and a curing agent, such as a trifunctional polyol, a tetrafunctional polyol, or a diamine. U.S. Pat. No. 5,334,673 discloses the use of two categories of polyurethane available on the market, i.e., thermoset and thermoplastic polyurethanes, for forming golf ball covers and, in particular, thermoset polyurethane covered golf balls made from a composition of polyurethane prepolymer and a slow-reacting amine curing agent and/or a difunctional glycol.

Unlike SURLYN® ionomer covered golf balls, polyurethane golf ball covers can be formulated to possess a softer "feel" like balata covered golf balls. However, golf ball covers made from polyurethane have not, to date, fully matched SURLYN® golf balls with respect to resilience or the rebound of a balata golf ball cover, which is a function of the initial velocity of a golf ball after impact with a golf club.

U.S. Pat. No. 3,989,568 discloses a three-component system employing either one or two polyurethane prepolymers and one or two polyol or fast-reacting diamine curing agents. The reactants chosen for the system must have different rates of reactions within two or more competing reactions.

U.S. Pat. No. 4,123,061 discloses a golf ball made from a polyurethane prepolymer of polyether and a curing agent, such as a trifunctional polyol, a tetrafunctional polyol, or a fast-reacting diamine curing agent.

U.S. Pat. No. 5,334,673 discloses a golf ball cover made from a composition of a thermosetting polyurethane prepolymer and a slow-reacting polyamine curing agent and/or a difunctional glycol. Resultant golf balls are found to have improved shear resistance and cut resistance compared to covers made from balata or SURLYN®.

U.S. Pat. No. 5,692,974 discloses methods of using cationic ionomers in golf ball cover compositions. Additionally, the patent relates to golf balls having covers and cores incorporating urethane ionomers. Improved resiliency and initial velocity are achieved by the addition of an alkylating agent, such as t-butyl-chloride, which induces ionic interactions in the polyurethane to produce cationic type ionomers.

PCT Publication WO 98/37929 discloses a composition for golf ball covers that includes a blend of a diisocyanate/polyol prepolymer and a curing agent comprising a blend of a slow-reacting diamine and a fast-reacting diamine. Improved "feel," playability, and durability characteristics are exhibited.

U.S. Pat. No. 5,976,034 discloses a composition for a multi-layer, wound golf ball that have a solid center and a thermoplastic intermediate layer that form a dual layer core, rubber thread windings, and a thermoplastic cover. These golf balls are said to possess high initial velocity at low head speed region and excellent flight performance, without compromising shot "feel."

U.S. Pat. No. 6,056,650 discloses a multi-piece golf ball having a solid core and a multi-layer cover having at least three layers, where the innermost cover layer and the outermost cover layer differ in hardness by not more than 3 Shore D units. These golf balls are said to possess increased flight distance when hit over a broad range of head speeds with any type of club, while maintaining feel, control, and durability.

Golf ball manufacturers are continually searching for new ways in which to provide wound golf balls that deliver the maximum performance for golfers. It would be advantageous to provide such a wound golf ball having improved playing characteristics.

SUMMARY OF THE INVENTION

The present invention is directed to a wound golf ball having at least four layers and a construction that can be tailored to possess the desired mix of characteristics of solid and wound golf balls. The performance of such a golf ball can be improved by altering the composition and/or nature of the materials and construction of the golf ball, as described below.

The present invention further relates to a multi-layer, wound golf ball comprising a center, at least one intermediate layer disposed over the center, a wound layer of a tensioned thread material disposed over the at least one intermediate layer, and a cover disposed over the wound layer, wherein at least one of the cover or the at least one intermediate layer may include a component that contains a thermoset material. In one embodiment, the center is solid, while in another embodiment the center is fluid-filled. Preferably, when the component includes a thermoset material and is present in the at least one intermediate layer or in the cover, the Shore D hardness of such layer is typically from about 30 to 85, more preferably from about 40 to 75, most preferably from about 50 to 65. In one embodiment, the difference in Shore D hardness between the outermost of the intermediate layers and the outermost cover layer may advantageously be less than about 10, preferably less than about 5, more preferably less than about 3.

Advantageously, the golf ball may include a cover having at least one of a dimple coverage of greater than about 60 percent, a hardness from about 30 to 85 Shore D, or a flexural modulus of greater than about 500 psi (3.4 MPa), and the golf ball has at least one of a compression from about 50 to 120 or a coefficient of restitution of greater than about 0.7.

The center of the golf ball may advantageously include one or more layers of polybutadiene, natural rubber, polyisoprene, styrene-butadiene copolymers, styrene-propylene-diene copolymers, or copolymers or mixtures thereof. Preferably, the diameter of the center can measure at least about 1 inch (25 mm), more preferably from about 0.9 inches (23 mm) to 1.5 inches (38 mm).

Additionally, the tensioned thread material of the wound layer may include fiber, glass, carbon, polyether urea, polyether block copolymers, polyester urea, polyester block copolymers, isotactic-poly(propylene), polyethylene, polyamide, poly(oxymethylene), polyketone, poly(ethylene terephthalate), poly(p-phenylene terephthalamide), poly (acrylonitrile), diaminodicyclohexylmethane, dodecanedicarboxylic acid, natural rubber, polyisoprene rubber, styrene-butadiene copolymers, styrene-propylene-diene copolymers, another synthetic rubber, or block, graft, random, alternating, brush, multi-arm star, branched, or dendritic copolymers, or combinations thereof. It should be understood that "combinations" of materials can include copolymers of those materials, as well as mere mechanical mixtures.

In one preferred embodiment, the thread material may include polyether urea, natural rubber, cis-polyisoprene, or mixtures thereof. In one more preferred embodiment, the thread material can include a polyether urea. Alternately, the thread material can include a blend of synthetic rubber and natural rubber. In the latter case, the synthetic rubber can include a mixture of at least two cis-1,4-polyisoprenes. Preferably, the synthetic polyisoprenes and the natural rubber in this embodiment may be present in amounts of at least about 60% and less than 40%, respectively, but more preferably, the synthetic polyisoprenes have a cis-1,4 content of at least 90%. It can be advantageous for the wound layer thickness to be less than 1 mm, especially where the thread material includes polyether urea. In other embodiments, the wound layer thickness may be less than 8 mm, preferably from about 0.9 mm to 8 mm.

In one preferred embodiment, the component includes at least two thermoset materials. In another preferred embodiment, the component includes at least one thermoset material and is substantially free of thermoplastic material, preferably entirely free of thermoplastic material.

Additionally, it is preferable that the at least one intermediate layer include a thermoset material, while the cover includes a thermoplastic material. Alternately, it is preferable that the cover include a thermoset material, while the at least one intermediate layer includes a thermoplastic material.

In another preferred embodiment, both the at least one intermediate layer and the cover each include a thermoset material, preferably the same thermoset material. Preferably, the cover contains a single layer.

Another aspect of the present invention relates to a multi-layer, wound golf ball comprising a center, at least one intermediate layer disposed over the center, a wound layer of a tensioned thread material disposed over the at least one intermediate layer, and a cover disposed over the wound layer, wherein the tensioned thread material can include fiber, glass, carbon, polyether urea, polyether block copolymers, polyester urea, polyester block copolymers, isotactic-poly(propylene), polyethylene, polyamide, poly (oxymethylene), polyketone, poly(ethylene terephthalate), poly(p-phenylene terephthalamide), poly(acrylonitrile), diaminodicyclohexylmethane, dodecanedicarboxylic acid, or block, graft, random, alternating, brush, multi-arm star, branched, or dendritic copolymers or mixtures thereof. Preferably, the thread material may include polyether urea. In other preferred embodiments, the wound layer thickness can be less than about 8 mm, preferably from about 0.9 mm to 8 mm. It can be advantageous for the wound layer thickness to be less than 1 mm, especially where the thread material includes polyether urea.

Advantageously, at least one of the cover or the at least one intermediate layer may include a component that contains a thermoset material.

The present invention also relates to a multi-layer, wound golf ball comprising a center, at least one intermediate layer disposed over the center, a wound layer of a tensioned thread material disposed over the at least one intermediate layer and having a thickness of less than about 1 mm, and a cover disposed over the wound layer.

In one embodiment, the tensioned thread material includes fiber, glass, carbon, polyether urea, polyether block copolymers, polyester urea, polyester block copolymers, isotactic-poly(propylene), polyethylene, polyamide, poly (oxymethylene), polyketone, poly(ethylene terephthalate), poly(p-phenylene terephthalamide), poly(acrylonitrile), diaminodicyclohexylmethane, dodecanedicarboxylic acid, natural rubber, polyisoprene rubber, styrene-butadiene copolymers, styrene-propylene-diene copolymers, another synthetic rubber, or block, graft, random, alternating, brush, multi-arm star, branched, or dendritic copolymers, or combinations thereof.

Further preferred embodiments may include, but are not limited to, any combination or permutation of aspects or qualities of the present invention listed above.

BRIEF DESCRIPTION OF THE DRAWINGS

Further features and advantages of the invention can be ascertained from the following detailed description that is provided in connection with the drawings described below:

FIG. **1** is a cross-section of a golf ball having a cover, and having an intermediate layer between a wound layer and a center, according to the invention.

DEFINITIONS

The term "about," as used herein, should be understood to refer to both numbers in a range of numbers.

As used herein, the term "Atti compression" is defined as the deflection of an object or material relative to the deflection of a calibrated spring, as measured with an Atti Compression Gauge, that is commercially available from Atti Engineering Corp. of Union City, N.J. Atti compression is typically used to measure the compression of a golf ball. When the Atti Gauge is used to measure cores having a diameter of less than 1.68 inches (43 mm), it should be understood that a metallic or other suitable shim is used to make the measured object approximately 1.68 inches (43 mm) in diameter.

As used herein, the term "coefficient of restitution" ("CoR") for golf balls is defined as the ratio of the rebound velocity to the inbound velocity when balls are fired into a rigid plate. The inbound velocity is understood to be 125 ft/s (38.1 m/s).

As used herein, the term "substantially free" means less than about 5 weight percent, preferably less than about 3 weight percent, more preferably less than about 1 weight percent, and most preferably less than about 0.01 weight percent.

The term "fluid," as used herein, includes gases, liquids, pastes, gels, or any combination thereof. Useful gases are

typically minimally reactive and may preferably include nitrogen or air. It should also be understood that, as used herein, a fluid-filled component may also be hollow or contain at least a partial vacuum.

As used herein, the terms "polymer" and "polymeric material" include amorphous, semi-crystalline, or crystalline polymers, and mixtures thereof, including, for example, random and block copolymers, rubbers, thermosets, thermoplastics, thermoplastic elastomers, and the like.

As used herein, the term "copolymer" should be understood to mean any block, graft, random, alternating, brush, multi-arm star, branched, dendritic, or other type of copolymer having two or more repeating units that is available to one of ordinary skill in the art.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is directed to a wound golf ball having at least four layers, where at least one wound layer is disposed over at least one intermediate layer, which is disposed over a center. A cover is then disposed over the wound layer. In one embodiment, at least one of the at least one intermediate layer and the cover includes a thermoset material. In a preferred embodiment, the at least one intermediate layer includes at least one thermoset material. In another preferred embodiment, the cover includes at least one thermoset material. In yet another preferred embodiment, the at least one intermediate layer and the cover each include at least one thermoset material. This at least one thermoset material can be the same thermoset material or a different material for each layer.

The golf ball according to the invention includes a center about which at least one intermediate layer is disposed. The center may be fluid or solid, but is preferably solid. In either case, the center is prepared using any material available to those of ordinary skill in the art, for example, such as a mixture of base rubber, a crosslinking agent, and optionally a free-radical initiator and/or filler(s). Examples of solid center materials include solid rubber, solid thermoplastic material, cork, wood, metal, or any combination thereof. Suitable fluid components in this embodiment may include, but are not limited to: air, water, corn syrup solids, salts, sugars and sugar derivatives, polymers and copolymers, and other water activity reducing agents. Typically, fluid-filled centers include at least one of the listed components, are hollow, or contain at least a partial vacuum.

Center layers of golf balls formed according to the invention are typically made from one or more elastomeric materials, as noted above. The base rubber can typically include natural or synthetic rubbers. A preferred base rubber is 1,4-polybutadiene. Natural rubber, polyisoprene rubber and/or styrene-butadiene rubber may be optionally combined with the 1,4-polybutadiene. Alternatively, the center can be made of multiple layers.

A representative base composition for forming the solid golf ball center 1, which includes at least one layer, formed of at least polybutadiene and, in parts by weight based on 100 parts polybutadiene, 0–50 parts of a metal salt diacrylate, dimethacrylate, or monomethacrylate, preferably zinc diacrylate, 0.01 to 5 parts by weight of an organic peroxide, and optionally 0 to 50 parts by weight of a filler. Suitable commercial sources of polybutadiene include Cariflex BR1220 manufactured by Shell Chemical of Houston, Tex., Neocis BR40 manufactured by Enichem Elastomers of Houston, Tex., and Ubepol BR150 manufactured by Ube Industries, Ltd. of Ube, Japan.

The at least one intermediate layer of the present invention can include any suitable materials known to those of ordinary skill in the art, including one or more thermoplastic and/or thermosetting materials. Advantageously, the at least one intermediate layer can include thermosetting polyurethanes or thermoplastic ionic copolymers, such as ionic copolymers of ethylene and an unsaturated monocarboxylic acid, commercially available under the SURLYN family of materials from E.I. DuPont de Nemours & Co., of Wilmington, DE, or IOTEK or ESCOR of Exxon of Irving, Tex. These are copolymers of ethylene and methacrylic acid or acrylic acid partially neutralized with salts of zinc, sodium, lithium, magnesium, potassium, calcium, manganese, nickel, or the like, or blends thereof, in which the salts are the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially neutralized and might include, for example, methacrylic, crotonic, maleic, fumaric or itaconic acid. However, any neutralized copolymer may be used in the golf balls of the present invention. In one preferred embodiment, the at least one intermediate layer and the center comprise different materials.

The golf balls of the present invention can likewise include one or more homopolymeric or copolymeric thermoplastic or thermoset materials in the at least one intermediate layer. One of ordinary skill in the art would know that most of the polymeric materials listed below may belong in the thermoplastic category or in the thermoset category, depending upon the nature of the repeat units, functional groups pendant from the repeat units, method of polymerization, method of formation, temperature of formation, post-polymerization treatments, and/or many other possible factors. The materials include, but are not limited to, the following:

(1) Vinyl resins, for example, such as those formed by the polymerization of vinyl chloride, or by the copolymerization of vinyl chloride with vinyl acetate, acrylic esters or vinylidene chloride;

(2) Polyolefins, for example, such as polyethylene, polypropylene, polybutylene, and copolymers, such as ethylene methylacrylate, ethylene ethylacrylate, ethylene vinyl acetate, ethylene methacrylic acid, ethylene acrylic acid, or propylene acrylic acid, as well as copolymers and homopolymers produced using a single-site catalyst;

(3) Polyurethanes, for example, such as those prepared from diols, triols, or polyols and diisocyanates, triisocyanates, or polyisocyanates, as well as those disclosed in U.S. Pat. No. 5,334,673;

(4) Polyureas, for example, such as those prepared from diamines, triamines, or polyamines and diisocyanates, triisocyanates, or polyisocyanates, as well as those disclosed in U.S. Pat. No. 5,484,870;

(5) Polyamides, for example, such as poly(hexamethylene adipamide) and others prepared from diamines and dibasic acids, as well as those from amino acids such as poly(caprolactam), and blends of polyamides with SURLYN, polyethylene, ethylene copolymers, ethyl-propylene-non-conjugated diene terpolymer, and the like;

(6) Acrylic resins and blends of these resins with, for example, polymers such as poly vinyl chloride, elastomers, and the like;

(7) Olefinic rubbers, for example, such as blends of polyolefins with ethylene-propylene-non-conjugated

diene terpolymer; block copolymers of styrene and butadiene, isoprene or ethylene-butylene rubber; or copoly(ether-amide), such as PEBAX, sold by ELF Atochem of Philadelphia, Pa.;

(8) Polyphenylene oxide resins or blends of polyphenylene oxide with high impact polystyrene, for example, as sold under the trademark NORYL by General Electric Company of Pittsfield, Mass.;

(9) Polyesters, for example, such as polyethylene terephthalate, polybutylene terephthalate, polyethylene terephthalate/glycol modified and elastomers, such as sold under the trademarks HYTREL by E.I. DuPont de Nemours & Co. of Wilmington, Del., and LOMOD by General Electric Company of Pittsfield, Mass.;

(10) Blends and alloys, for example including polycarbonate with acrylonitrile butadiene styrene, polybutylene terephthalate, polyethylene terephthalate, styrene maleic anhydride, polyethylene, elastomers, and the like, and polyvinyl chloride with acrylonitrile butadiene styrene, ethylene vinyl acetate, or other elastomers;

(11) Blends of vulcanized, unvulcanized, or non-vulcanizable rubbers with polyethylene, propylene, polyacetal, nylon, polyesters, cellulose esters, and the like; and

(12) Polymers or copolymers possessing epoxy-containing, or post-polymerization epoxy-functionalized, repeat units, for example, in combination with anhydride, ester, amide, imide, carbonate, ether, urethane, urea, -olefin, conjugated, or acid (optionally totally or partially neutralized with inorganic salts) comonomers, or copolymers or blends thereof.

The at least one intermediate layer may also contain polymers such as ethylene, propylene, and other 1-alkylene based homopolymers and copolymers, including functional monomers such as acrylic and methacrylic acid and fully or partially neutralized ionomer resins and their blends, methyl acrylate, methyl methacrylate homopolymers and copolymers, imidized, amino group containing polymers, polycarbonate, reinforced polyamides, polyphenylene oxide, high impact polystyrene, polyether ketone, polysulfone, poly(phenylene sulfide), acrylonitrile-butadiene, acrylic-styrene-acrylonitrile, poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene vinyl alcohol), poly(tetrafluoroethylene) and their copolymers including functional comonomers and blends thereof. One exemplary material for use in the at least one intermediate layer, preferably in blends with ionomer(s), such as SURLYN®, is a non-ionomeric, maleic anhydride-grafted, ethylene-butylene metallocene-catalyzed polymer. This material has been commercially available, for example, under the name FUSABOND 525D or SURLYN® NMO 525D, from E.I. DuPont de Nemours & Co. of Wilmington, Del. The at least one intermediate layer may further include a polyether or polyester thermoplastic urethane, a thermoset polyurethane, or an ionomer, for example, such as acid-containing ethylene copolymer ionomers, including E/X/Y terpolymers where E is ethylene, X is an acrylate- or methacrylate-based comonomer present in 0 to 50 weight percent and Y is acrylic or methacrylic acid present in 5 to 35 weight percent.

In those embodiments wherein the at least one intermediate layer of the golf ball is formed with a thermoset material, for example, such as a polyurethane, the layer may be molded onto the unfinished ball in accordance with the teaching of U.S. Pat. Nos. 5,733,428 and 5,888,437, without, of course, the step(s) associated with forming dimples. Preferably, the at least one intermediate layer can include thermosetting polyurethanes.

In one preferred embodiment, when the component present in at least one of the at least one intermediate layer or the cover includes a thermoset material, the thermoset material may be present in an amount greater than about 10 weight percent of the total polymer in the given layer, preferably in an amount greater than about 50 weight percent, more preferably in an amount greater than about 90 weight percent, most preferably in an amount such that the given layer is substantially free of thermoplastic polymer material.

In another embodiment, the at least one intermediate layer can possess a Shore D hardness from about 30 to 52, preferably from about 35 to 50, as measured on the unfinished ball after disposition of the at least one intermediate layer. In yet another embodiment, the thickness of the at least one intermediate layer can be greater than about 0.65 cm.

The wound layer is typically disposed about the at least one intermediate layer and includes a tensioned thread material. Many different kinds of thread materials may be used for the wound layer of the present invention. The thread may be single-ply or may include two or more plies. Preferably, the thread of the present invention is single-ply. The thread may be selected to have varied material properties, dimensions, cross-sectional shapes, and methods of manufacturing. If two or more threads are used, they may be identical in material and mechanical properties or they may be substantially different from each other, either in cross-section shape or size, composition, elongated state, and mechanical or thermal properties. Mechanical properties that may be varied include, but are not limited to, resiliency, elastic modulus, and density. Thermal properties that may be varied include, but are not limited to, melt temperature, glass transition temperature, and thermal expansion coefficient.

The tensioned thread material of the wound layer typically includes fiber, glass, carbon, polyether urea, polyether block copolymers, polyester urea, polyester block copolymers, isotactic-poly(propylene), polyethylene, polyamide, poly(oxymethylene), polyketone, poly(ethylene terephthalate), poly(p-phenylene terephthalamide), poly (acrylonitrile), diaminodicyclohexylmethane, dodecanedicarboxylic acid, natural rubber, polyisoprene rubber, styrene-butadiene copolymers, styrene-propylene-diene copolymers, another synthetic rubber, or block, graft, random, alternating, brush, multi-arm star, branched, or dendritic copolymers, or mixtures thereof. For example, the tensioned thread material of the wound layer may include a polymeric material such as Hytrel®, a polyetherester commercially available from E.I. DuPont de Nemours of Wilmington, Del. Preferred thread materials are elastomeric, while graphite thread tends to be less preferred than other available thread types due to the difficulty in placing such threads under tension when being wound about a center. A preferred thread material includes polyether urea. Preferably, in one embodiment, the wound layer can be substantially free of polyisoprene, natural rubber, and/or other rubbers. More preferably, the wound layer is entirely free of polyisoprene and/or natural rubber. Another exemplary thread material is a mixture of cis-polyisoprene and natural rubbers, preferably at least about 60% of a blend of two or more synthetic cis-1,4 polyisoprene rubbers, and about less than 40% of a natural rubber component. It is preferred that the synthetic cis-1,4 polyisoprene rubbers have a cis-isomer content of at least 90%, however the cis-isomer content may vary for each rubber.

The thickness of the wound layer will typically be not more than about 8 mm, preferably from about 0.9 mm to 8 mm thick. More preferably, the thickness of the wound layer is less than 1 mm.

Threads used in the present invention may be formed using a variety of processes including conventional calendering and slitting, melt spinning, wet spinning, dry spinning and polymerization spinning. Any process available to one of ordinary skill in the art may be employed to produce thread materials for use in the wound layer. The tension used in winding the thread material of the wound layer may be selected as desired to provide beneficial playing characteristics to the final golf ball. The winding tension and elongation may be kept the same or may be varied throughout the layer. Preferably, the winding occurs at a consistent level of tension so that the wound layer has consistent tension throughout the layer.

In addition, the winding patterns used for the wound layer can be varied in any way available to those of ordinary skill in the art. Although one or more threads may be combined to begin forming the wound layer, it is preferred to use only a single continuous thread.

The cover provides the interface between the ball and a club. Properties that are desirable for the cover include good moldability, high abrasion resistance, high tear strength, high resilience, and good mold release, among others. The cover typically provides good performance characteristics and durability. The cover of the golf ball typically has a thickness of at least about 0.075 cm. In one embodiment, the cover has a thickness from at least about 0.075 cm to 0.36 cm.

The cover of the present invention can include any suitable materials described above for the at least one intermediate layer. In those embodiments wherein the cover of the golf ball includes a thermoset material, for example, such as a polyurethane, the layer may be molded onto the unfinished ball in accordance with the teaching of U.S. Pat. Nos. 5,733,428 and 5,888,437, with, or optionally without, the step(s) associated with forming dimples. Preferably, the cover can include thermosetting polyurethanes.

In another embodiment, the cover can possess a Shore D hardness from about 30 to 52, preferably from about 35 to 50, as measured on the ball after disposition of the cover. In one preferred embodiment, the cover is a single layer.

To clarify the scope of the invention, a golf ball made according to the invention has at least four layers including a center, at least one intermediate layer, a wound layer, and a cover. From this basic construct, there are three major aspects of the present invention: (1) at least one of the at least one intermediate layer and the cover includes a component containing a thermoset material; (2) the wound layer contains a tensioned thread material that includes fiber, glass, carbon, polyether urea, polyether block copolymers, polyester urea, polyester block copolymers, isotactic-poly (propylene), polyethylene, polyamide, poly(oxymethylene), polyketone, poly(ethylene terephthalate), poly(p-phenylene terephthalamide), poly(acrylonitrile), diaminodicyclohexylmethane, dodecanedicarboxylic acid, or combinations thereof; and (3) the wound layer has a thickness less than 1 mm.

The first aspect of the invention can be broken down into three major categories of golf balls, having: (a) thermoplastic material in the at least one intermediate layer with thermoset material in the cover; (b) thermoset material in the at least one intermediate layer with thermoplastic material in the cover; and (c) thermoset material in both the at least one intermediate layer and the cover. The center of these golf balls may embody various constructions, as may the tensioned thread winding in the wound layer.

The second aspect of the invention specifies certain types of materials as the tensioned thread material of the wound layer. The center of these golf balls can embody various constructions. Also, although the at least one intermediate layer and the cover layer can embody various constructions, the second aspect of the invention may incorporate the three major categories of the first aspect of the invention, as well as the case where both the at least one intermediate layer and the cover contain only thermoplastic material.

The third aspect of the invention specifies a certain thickness of the wound layer. The center of these golf balls may embody various constructions. Also, although the tensioned thread material can embody various constructions, the third aspect of the invention may incorporate the winding materials specified in the second aspect of the invention, as well as including other materials, such as synthetic polyisoprene and/or natural rubber. Additionally, although the at least one intermediate layer and the cover layer can embody various constructions, the third aspect of the invention may incorporate the three major categories of the first aspect of the invention, as well as the case where both the at least one intermediate layer and the cover contain only thermoplastic material.

A free-radical source, often alternatively referred to as a free-radical initiator, may optionally be used in one or more layers of the golf balls according to the invention, particularly when the polymer component includes a thermoset material. The free-radical source is typically a peroxide, and preferably an organic peroxide. Suitable free-radical sources include di-t-amyl peroxide, di(2-t-butyl-peroxyisopropyl) benzene peroxide, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, dicumyl peroxide, di-t-butyl peroxide, 2,5-di-(t-butylperoxy)-2,5-dimethyl hexane, n-butyl-4,4-bis(t-butylperoxy)valerate, lauryl peroxide, benzoyl peroxide, t-butyl hydroperoxide, and the like, and any mixture thereof. The peroxide is typically present in an amount greater than about 0.1 parts per hundred of the total polymer component, preferably about 0.1 to 15 parts per hundred of the polymer component, and more preferably about 0.2 to 5 parts per hundred of the total polymer component. It should be understood by those of ordinary skill in the art that the presence of certain components may require a larger amount of free-radical source than the amounts described herein. The free radical source may alternatively or additionally be one or more of an electron beam, UV or gamma radiation, x-rays, or any other high energy radiation source capable of generating free radicals. It should be further understood that heat often facilitates initiation of the generation of free radicals when peroxides are used as a free-radical initiator.

Crosslinking agents may also optionally be included in one or more layers of the golf ball according to the invention. Again, these are optional but preferred, particularly when the polymer component of a layer includes at least one thermoset material. Suitable crosslinking agents can include one or more metallic salts of unsaturated fatty acids or monocarboxylic acids, such as zinc, calcium, or magnesium acrylate salts, and the like, and mixtures thereof. Preferred acrylates include zinc acrylate, zinc diacrylate, zinc methacrylate, and zinc dimethacrylate, and mixtures thereof. The crosslinking agent, when included, should be present in an amount sufficient to crosslink a portion of the chains of polymers in the polymer component. For example, the desired compression may be obtained by adjusting the amount of crosslinking. This may be achieved, for example,

by altering the type and amount of crosslinking agent, a method well-known to those of ordinary skill in the art. The crosslinking agent, when used is typically present in an amount greater than about 0.1 weight percent of the polymer component, preferably from about 10 to 40 weight percent of the polymer component, more preferably from about 10 to 30 weight percent of the polymer component.

Fillers added to one or more layers of the golf ball typically include processing aids or compounds to affect Theological and mixing properties, the specific gravity (i.e., density-modifying fillers), the modulus, the tear strength, reinforcement, and the like. A density adjusting filler may be used to control the moment of inertia, and thus the initial spin rate of the ball and spin decay. For example, fillers may be present in an amount from about 0.1 to 50 weight percent of a given layer.

Fillers are typically polymeric or inorganic in nature, and, when used, are typically present in an amount from about 0.1 to 50 weight percent of the layer in which they are included. Any suitable filler available to one of ordinary skill in the art may be used. Exemplary fillers include, but are not limited to, precipitated hydrated silica; clay; talc; asbestos; glass fibers; aramid fibers; mica, calcium metasilicate; barium sulfate; zinc sulfide; lithopone; silicates; silicon carbide; diatomaceous earth; polyvinyl chloride; carbonates such as calcium carbonate and magnesium carbonate; metals such as titanium, tungsten, aluminum, bismuth, nickel, molybdenum, iron, lead, copper, boron, cobalt, beryllium, zinc, and tin; metal alloys such as steel, brass, bronze, boron carbide whiskers, and tungsten carbide whiskers; metal oxides such as zinc oxide, iron oxide, aluminum oxide, titanium oxide, magnesium oxide, tungsten oxide, lead oxides, and zirconium oxide; particulate carbonaceous materials such as graphite, carbon black, cotton flock, natural bitumen, cellulose flock, and leather fiber; micro balloons such as glass and ceramic; fly ash; cured, ground rubber; or combinations thereof.

Fillers may also include various foaming agents or blowing agents which may be readily selected by one of ordinary skill in the art. Foamed polymer blends may be formed by blending ceramic or glass microspheres with polymer material. Polymeric, ceramic, metal, and glass microspheres may be solid or hollow, and filled or unfilled. Fillers are typically also added to one or more portions of the golf ball to modify the density thereof to conform to uniform golf ball standards. Fillers may also be used to modify the weight of the center or at least one additional layer for specialty balls, e.g., a lower weight ball is preferred for a player having a low swing speed.

Additionally, certain polymeric materials, such as unvulcanized polybutadiene rubber, in one or more layers of the golf balls prepared according to the invention typically have a Mooney viscosity greater than about 20, preferably greater than about 30, and more preferably greater than about 40. Mooney viscosity is typically measured according to ASTM D-1646.

The resultant golf balls prepared according to the invention typically will have dimple coverage greater than about 60 percent, preferably greater than about 65 percent, and more preferably greater than about 70 percent. The golf balls typically have a coefficient of restitution of greater than about 0.7, preferably greater than about 0.75, and more preferably greater than about 0.78. The golf balls also typically have an Atti compression of at least about 40, preferably from about 50 to 120, and more preferably from about 60 to 100. The golf ball polybutadiene material of the present invention typically has a flexural modulus of from about 500 psi (3.4 MPa) to 300,000 psi (2.1 GPa), preferably from about 2000 psi (13.7 MPa) to 200,000 psi (1.4 GPa). The golf ball polybutadiene material typically has a hardness of at least about 15 Shore A, preferably between about 30 Shore A and 80 Shore D, more preferably between about 50 Shore A and 60 Shore D. The specific gravity is typically greater than about 0.7, preferably greater than about 1, for the golf ball polybutadiene material.

Any size golf ball may be formed according to the invention, although the golf ball preferably meets USGA standards of size and weight. For example, the final golf ball should typically have an outer diameter of greater than about 1.67 inches (42 mm), preferably from about 1.67 inches (42 mm) to 1.74 inches (44 mm), more preferably of about 1.68 inches (43 mm).

Referring to FIG. **1**, a wound golf ball of the present invention includes a center **1** having at least one layer, at least one intermediate layer **2** disposed over the center **1**, a wound layer **3** disposed over the at least one intermediate layer **2**, and a cover **4** disposed over the wound layer **3**. The combination of the center **1** and each intermediate layer **2** (only one layer depicted) form the core of the golf ball. The cover **4** is shown as a single layer. The cover can have more than one layer, of course, such as in a two-layer cover construction (not shown) where the first cover layer surrounds the wound layer **3** and the second cover layer surrounds the first layer.

EXAMPLES

Certain embodiments of the present invention are illustrated by reference to the following examples:

Examples 1–2

Golf Ball Cores Before Winding Layer Applied

Golf ball cores, before the winding layer is applied, that combined solid, unitary rubber centers with an intermediate layer of either a thermoplastic ionomer resin or a thermoplastic resin were prepared according to the invention. The properties of the centers and cores, i.e., one intermediate layer disposed over the center, are listed in Table 1.

The intermediate layer of each of Examples 1–2 was injection molded over each center. In these Examples, the ionomer thermoplastic material was a blend of SURLYN ionomers, and the thermoplastic material was a blend including FUSABOND 525D, also called SURLYN NMO 525D, with one or more SURLYN ionomers, all available from E.I. DuPont de Nemours & Co., of Wilmington, Del.

TABLE 1

	Diameter (in.)	Atti Comp.	CoR (@ 125 ft/s)	Specific Gravity
Center	1.39	68	0.791	1.14
Core	Diameter (in.)	Atti Comp.	CoR (@ 125 ft/s)	Hardness (Shore D)
Example 1: With Ionomer Thermoplastic Intermediate Layer	1.51	86	0.808	64
Example 2: With Thermoplastic Intermediate Layer	1.51	81	0.802	59

Examples 3–8

Multi-Layer Wound Golf Balls According to the Present Invention

The spin tests conducted on the golf balls of these examples, e.g., Standard Driver Spin, Average Driver Spin,

8-Iron Spin, and ½-Wedge Spin, were conducted under the conditions set forth in Table 2. In order to standardize such spin tests, the testing equipment for each club type was calibrated with a selected commercial ball to obtain a desired spin rate, as demonstrated for each test in Table 2. The Pinnacle Gold® and Tour Balata® golf balls used to calibrate the equipment are available from Acushnet Company of Fairhaven, Mass. These setup conditions were used for testing balls prepared according to the invention and for comparative testing for each club type listed in Tables 3 &4.

TABLE 2

Spin test	Calibration Ball	Launch angle	Ball speed	Spin Rate
Standard Driver	Pinnacle Gold ®	9.5°	160 mph	3000 rpm
Average Driver	Pinnacle Gold ®	10.5°	140 mph	3600 rpm
8-Iron	Tour Balata ®	18.5°	115 mph	9000 rpm
½-Wedge	Tour Balata ®	32°	52 mph	7200 rpm

The multi-layer, wound golf balls of Examples 3–8 were prepared using the center of Examples 1–2. The intermediate layer in Examples 3–8 was chosen from a polymer including an ionomer thermoplastic resin or a thermoplastic resin, or a blend thereof, as noted in Table 3.

A wound layer was disposed on each of the cores. The windings for the golf balls of Examples 3–8 were made of a polyether urea thread, sold under the LYCRA series, available from E.I. DuPont de Nemours & Co., of Wilmington, Del. The cover was then disposed over the wound layer. For cover of an ionomeric or other thermoplastic material, the thickness of the thread layer for each ball was approximately 0.95 mm. For covers with a urethane thermoset layer, the thickness of the thread layer for each ball was approximately 0.995 mm. In all balls of Examples 3–8, the outer diameter of the core plus the wound layer, reflected as an average of at least four measurements, was around 1.585 inches (40 mm).

The single cover layer in these examples, as shown in Table 3, was selected from thermoplastic or thermosetting materials, or blends thereof. "Blends" in this application are frequently referred to as being thermoset or thermosetting if they include a thermoset material.

Advantageously, the golf balls of Examples 3–6, which contain thermoplastic and/or ionomer thermoplastic formulations in the cover layers, compare favorably to the conventional golf ball of Example 9. As can be seen from Tables 3 & 4, the golf balls according to the invention of Examples 3–6 show comparable standard driver spin, average driver spin, and ½-wedge spin to the conventional golf ball of Example 9, while offering a distinct improvement in 8-iron spin.

Also, the golf balls of Examples 3 and 6 show modest increases in spin for all clubs tested, compared to the conventional golf ball of Example 10. This phenomenon is of particular interest because the covers on all three balls are made from the same material.

Spin ratios of standard or average Driver spin to 8-iron or to ½-wedge spin can additionally provide comparison between the golf balls according to the invention and golf balls of different construction. For driver-to-iron or driver-to-wedge ratios, it is particularly desirable that the spin ratio be comparatively low, since lower spin is considered more desirable for a driver and higher spin is considered more desirable for irons and wedges. Several differences in driver-to-iron and driver-to-wedge spin ratios exist between the golf balls according to the invention and selected golf balls of different construction.

The golf balls according to the invention have lower, and thus more desirable, spin ratios of driver to wedge and iron spin rates than the conventional golf balls of Examples 9, 11, and 12, while the golf balls prepared according to the invention have similar compression, hardness, and other properties.

Further, in comparison to the golf balls according to the invention, i.e., Examples 3–8, the conventional golf balls of Examples 11 and 12 exhibit significantly higher, and thus less desirable, driver-to-wedge spin ratios. This can seen very clearly across the board by examining the standard driver spins and to a lesser extent when considering the average driver spin ratios.

Examples 9–12

Comparative Examples of Golf Balls Possessing a Different Construction than According to the Invention

Examples 9–12 are conventional golf balls with different construction than the golf balls prepared according to the present invention. The properties of these balls are included for comparison and reference, as shown in Table 4.

Example 9 was a multi-layer golf ball with a polybutadiene core having a diameter of about 1.55 inches (39 mm). Disposed over the solid core was a thermoplastic inner cover layer, such that the diameter of the unfinished ball is about 1.62 inches (41 mm). An elastomeric urethane outer cover layer having a Shore D hardness of about 60 was disposed over the thermoplastic inner layer. Example 10 was also a multi-layer golf ball with a polybutadiene core having a diameter of about 1.43 inches (36 mm). Disposed over the solid core was a mantle layer composed of an Estane®/Hytrel® polymer blend, such that the diameter of the unfinished ball was about 1.55 inches (39 mm). A thermoplastic cover layer having a Shore D hardness of about 70 was disposed over the mantle layer. Example 11 was a wound golf ball with a liquid-filled Pebax® center having a diameter of about 1.13 inches (29 mm). A wound layer was disposed over the center, such that the diameter of the ball core was about 1.58 inches (40 mm). An elastomeric urethane cover layer was disposed over the wound core to form the golf ball of Example 11. Example 12 was also a wound golf ball, but with a liquid-filled rubber center having a diameter of about 1.125 inches (29 mm). A wound layer was disposed over the center such that the diameter of the ball core was about 1.6 inches (41 mm). A synthetic balata cover layer was disposed over the wound core to form the golf ball of Example 12.

It is to be understood that the invention is not to be limited to the exact configuration as illustrated and described herein. For example, it should be apparent that a variety of materials would be suitable for use in the composition or method of making the golf balls according to the Detailed Description of the Preferred Embodiments. Accordingly, all expedient modifications readily attainable by one of ordinary skill in the art from the disclosure set forth herein, or by routine experimentation therefrom, are deemed to be within the spirit and scope of the invention as defined by the appended claims.

TABLE 3

Intermediate Layer/Cover Layer	Atti Comp.	CoR (@ 125 ft/s)	Hardness (Shore D)	Std. Driver Spin (rpm)	Avg. Driver Spin (rpm)	8-Iron Spin (rpm)	1/2-Wedge Spin (rpm)
Example 3 Thermoplastic/Thermoplastic ionomer	104	0.798	66	3030	3780	7770	6290
Example 4 Thermoplastic/Thermoplastic	100	0.791	62	3160	3860	7630	6640
Example 5 Thermoplastic ionomer/Thermoplastic	103	0789	62	3190	3910	7610	6630
Example 6 Thermoplastic ionomer/Thermoplastic ionomer	108	0.793	66	3120	3860	7760	6230
Example 7 Thermoplastic ionomer/Thermoset urethane	101	0.784	55	3370	4080	7850	6870
Example 8 Thermoplastic/Thermoset urethane	98	0.786	55	3380	4060	7920	6820

TABLE 4

Comparative Golf Balls	Atti Comp.	CoR (@ 125 ft/s)	Hardness (Shore D)	Std. Driver Spin (rpm)	Avg. Driver Spin (rpm)	8-Iron Spin (rpm)	1/2-Wedge Spin (rpm)
Example 9 solid center, thermoplastic/thermoset inner/outer cover	94	0.798	59	3150	3740	6920	6620
Example 10 solid center, thermoplastic mantle & cover	85	0.800	69	2940	3550	7310	5860
Example 11 liquid center, wound ball, thermoset cover	101	0.792	57	3880	4590	8230	7010
Example 12 liquid center, wound ball, synthetic balata cover	94	0.793	50	4190	4910	8690	7200

What is claimed is:

1. A multi-layer, wound golf ball comprising:

a solid center formed of a thermoplastic elastomer;

at least one intermediate layer disposed over the center;

a wound layer of a tensioned material disposed over the at least one intermediate layer; and

a cover disposed over the wound layer;

wherein the at least one intermediate layer is formed from a component which comprises a thermoset material.

2. A multi-layer, wound golf ball comprising:

a solid center;

at least one intermediate layer disposed over the center;

a wound layer of a tensioned material disposed over the at least one intermediate layer; and

a cover disposed over the wound layer;

wherein the at least one intermediate layer is formed from a component which comprises a thermoset material; and

wherein the golf ball comprises a cover material having at least one of a dimple coverage of greater than about 60 percent, a hardness from about 30 to 85 Shore D, or a flexural modulus of greater than about 3.4 Mpa, and wherein the golf ball has at least one of a compression from about 50 to 120 or a coefficient of restitution of greater than about 0.7.

3. The golf ball of claim 2, wherein the outermost intermediate layer and the outermost cover layer each have a Shore D hardness from about 30 to 85.

4. The golf ball of claim 2, wherein the center comprises polybutadiene, natural rubber, polyisoprene, styrene-butadiene copolymers, styrene-propylene-diene copolymers, or combinations thereof.

5. The golf ball of claim 4, wherein the center has a diameter from about 0.9 inches (23 mm) to 1.5 inches (38 mm).

6. The golf ball of claim 2, wherein the wound layer has a thickness from about 0.9 mm to 8 mm.

7. The golf ball of claim 2, wherein the wound layer has a thickness less than 1 mm.

8. The golf ball of claim 2, wherein the component comprises at least one thermoset material and is substantially free of thermoplastic material.

9. The golf ball of claim 2, wherein the at least one intermediate layer comprises a thermoset material and the cover comprises a thermoplastic material.

10. The golf ball of claim 2, wherein the at least one intermediate layer and the cover each comprise a thermoset material.

11. The golf ball of claim 10, wherein the at least one intermediate layer and the cover comprise the same thermoset material.

12. The golf ball of claim 2, wherein the cover is a single layer.

13. The golf ball of claim 2, wherein the difference in Shore D hardness between the outermost of the intermediate layers and the outermost cover layer is less than about 5.

14. A multi-layer, wound golf ball comprising:

a solid center;

at least one intermediate layer disposed over the center;

a wound layer of a tensioned material disposed over the at least one intermediate layer; and

a cover disposed over the wound layer; and

wherein the at least one intermediate layer comprises a thermoplastic material; and

wherein the golf ball comprises a cover material having at least one of a dimple coverage of greater than about 60 percent, a hardness from about 30 to 85 Shore D, or a flexural modulus of greater than about 3.4 Mpa, and wherein the golf ball has at least one of a compression from about 50 to 120 or a coefficient of restitution of greater than about 0.7.

15. The golf ball of claim **14**, wherein the at least one intermediate layer comprises a thermoplastic ionic copolymer.

16. The golf ball of claim **14**, wherein the at least one intermediate layer comprises a totally neutralized copolymer.

17. The golf ball of claim **14**, wherein the cover comprises polyurethane.

18. The golf ball of claim **14**, wherein the layer of tensioned material has a thickness less than 1 mm.

19. A multi-layer, wound golf ball comprising:

a center;

at least one intermediate layer disposed over the center;

a wound layer of a tensioned material disposed over the at least one intermediate layer and having a thickness of less than 1 mm; and

a cover disposed over the wound layer;

wherein the tensioned material comprises polyether urea.

20. A multi-layer, wound golf ball comprising:

a center;

at least one intermediate layer disposed over the center;

a wound layer of a tensioned material disposed over the at least one intermediate layer and having a thickness of less than 1 mm; and

a cover disposed over the wound layer;

wherein at least one of the cover or the at least one intermediate layer is formed from a component which comprises a thermoset material.

21. The golf ball of claim **20**, wherein the at least one intermediate layer comprises a thermoset material and the cover comprises a thermoplastic material.

22. The golf ball of claim **20**, wherein the at least one intermediate layer comprises a thermoplastic material and the cover comprises a thermoset material.

23. The golf ball of claim **20**, wherein the at least one intermediate layer and the cover comprise a thermoset material.

24. The golf ball of claim **23**, wherein the at least one intermediate layer and the cover comprise the same thermoset material.

25. The golf ball of claim **20**, wherein the at least one intermediate layer is formed of a thermoplastic ionomer.

26. A multi-layer, wound golf ball comprising:

a fluid-filled center;

at least one intermediate layer disposed over the center;

a wound layer of a tensioned material disposed over the at least one intermediate layer; and

a cover disposed over the wound layer,

wherein the at least one intermediate layer is formed from a component which comprises a thermoset material.

27. The golf ball of claim **26**, wherein the outermost intermediate layer has a Shore D hardness from about 30 to 52.

28. The golf ball of claim **26**, wherein the center has a diameter from about 0.9 inches to 1.5 inches.

29. The golf ball of claim **26**, wherein the wound layer has a thickness from about 0.9 mm to 8 mm.

30. The golf ball of claim **26**, wherein the wound layer has a thickness less than 1 mm.

31. The golf ball of claim **26**, wherein the component comprises at least one thermoset material and is substantially free of thermoplastic material.

32. The golf ball of claim **26**, wherein the at least one intermediate layer comprises a thermoset material and the cover comprises a thermoplastic material.

33. The golf ball of claim **26**, wherein the at least one intermediate layer comprises a thermoplastic material and the cover comprises a thermoset material.

34. The golf ball of claim **26**, wherein the at least one intermediate layer and the cover each comprise a thermoset material.

35. The golf ball of claim **34**, wherein the at least one intermediate layer and the cover comprise the same thermoset material.

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